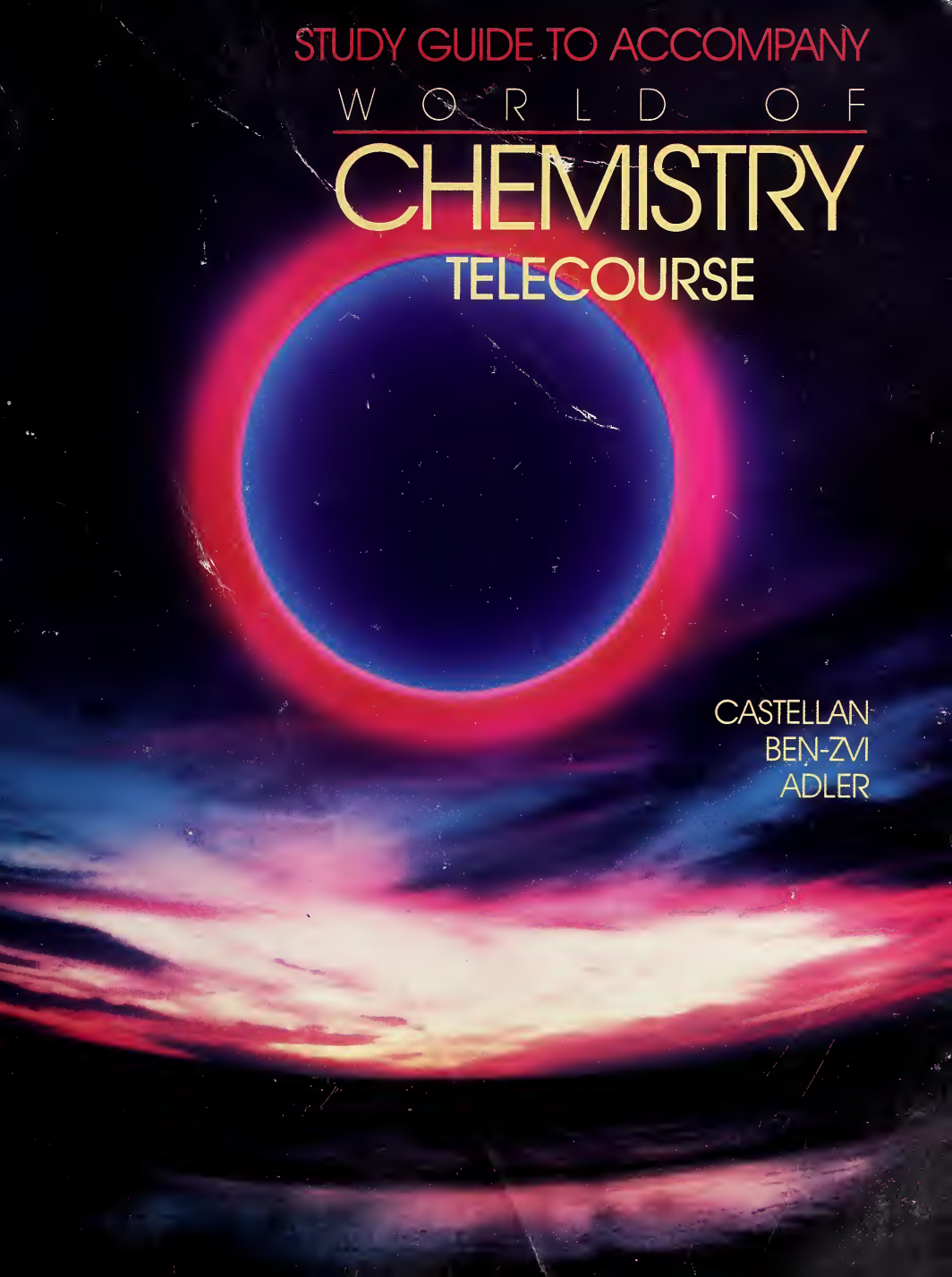
STUDY GUIDE TO ACCOMPANY

WORLD OF CHEMISTRY

TELECOURSE



CASTELLAN
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The World of Chemistry

Study Guide

Gilbert Castellan
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Saunders College Publishing
Harcourt Brace Jovanovich College Publishers
Fort Worth Philadelphia San Diego
New York Orlando Austin San Antonio
Toronto Montreal London Sydney Tokyo

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Printed in the United States of America.

Joesten: Study Guide to accompany THE WORLD OF CHEMISTRY

ISBN # 0-03-030172-6

2 066 9876543

The World of Chemistry Study Guide

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Introduction

This study guide aims to provide a consistent method of incorporating the television programs with the textbook. The textbook includes many more topics than are dealt with in the television programs. The Study Guide, on the other hand, is confined to the topics covered in the television programs. The 26 units of the Study Guide are wrapped around the 26 television programs.

In studying the material in this course, you may wish to use the following plan:

Begin by refreshing your mind on the things you already know. The Study Guide will prompt you on a few of the most pertinent of these items.

Read the sections of the textbook recommended in the Study Guide. If you are studying under the guidance of a teacher, additional readings may be assigned.

Read the sections of the Study Guide entitled "Overview" and "What to Look For". Then watch the program. After watching the program, study the rest of the material in the Study Guide.

STRUCTURE OF THE STUDY GUIDE

The Study Guide consists of this brief introduction and of 26 Units, each corresponding to one of the television programs. The Units are designed to help the student focus on the content of the programs and to develope the main points made in the programs in somewhat greater detail.

STRUCTURE OF THE UNITS IN THE STUDY GUIDE

Except for Units 1 and 26 which are very brief, the other 24 Units are structured in the following way:

THE TITLE

This is the same as the program title.

BEFORE WATCHING

This is the first main section of the Unit.

YOU ALREADY KNOW

This subsection draws your attention to a few concepts, definitions, laws, or phenomena that have already been learned and that are pertinent to the contents of this Unit.

READ

This subsection lists the titles of the sections of the chapters to be read. The reference is to the book, *The World of Chemistry*, by Melvin D. Joester et al. If the title is enclosed by quotation marks, it is the title of a section of a chapter. If the quotation marks are missing, it is the chapter title and the entire chapter should be read. Of course, the readings here should be done before viewing the program.

OVERVIEW

This subsection is a brief guide to the contents of the program.

WHAT TO LOOK FOR

This subsection lists the main points in the program in outline form.

WATCH THE PROGRAM

A direction to the student.

AFTER WATCHING

This is the second main section of the Unit. In this section the outline in **WHAT TO LOOK FOR** is fleshed out. The various points covered in the program are discussed and amplified somewhat. The material enclosed in boxes usually discusses things that were not explicitly covered in the program but are closely related to the program material.

HANDS ON

This section suggests simple observational activities that are related to topics in the program.

QUESTIONS

A few questions related to subjects covered in the program are presented here.

Acknowledgments

The authors wish to acknowledge the many people who helped to complete this study guide. We gained valuable suggestions and insights from Margot Schumm of Montgomery College, Rockville Campus Md, a member of the academic team for The World of Chemistry project who tried out the first draft of various units of the study guide. We owe special debt to the following individuals, institutes, and their students for field testing The World of Chemistry sample units and programs:

James D. Carr & Robert Harris	University of Nebraska, Lincoln, NE & Pius X High School, Lincoln, NE
Lavoir Banks	Elgin Community College, Elgin, IL
R. Hoots	Yuba College, Woodland, CA
Sandra Etheridge	Gulf Coast Community College, Panama City, FL
Larry Peck	Texas A&M University, College Station, TX
Jeanne Robinson	Seminole Community College, Sanford, FL
Ronald E. DiStefano	Northampton County Community College, Bethlehem, PA
Cynthia T. Hahn	Bristol Community College, Fall River, MA
Gary Trammell	Sangamon State University, Springfield, IL
Ray Johnson	Hillsdale College, Hillsdale, MI
John Fortman	Wright State University, Dayton, OH
Annie-Marie Kubanek	John Abbot College, Saint-Anne-de-Bellevue, Quebec, Canada
Wesley Smith	Ricks College, Rexburg, ID
Mary E. Key	St. Albans School, Washington, D.C.
Evan T. Williams	Brooklyn College, CUNY, NY, NY

We thank our production team, headed by the executive producer Richard Thomas, at the Education Film Center, for putting the television component together. We thank our project manager Lisa Ragsdale. Special thanks to our board of advisors for their generous gifts of time and expertise:

Dr. Gustaf Arrhenius	University of California, San Diego
Dr. Marjorie Gardner	University of California, Berkeley
Dr. Noel Hinners	National Aeronautics and Space Administration
Dr. J. Ivan Legg	Auburn University
Prof. Mitchell Lifton	University of Maryland at College Park
Dr. Paul Mazzocchi	University of Maryland at College Park
Dr. Eric Mendoza	Hebrew University of Jerusalem
Dr. William Mooney	El Camino College
Dr. David Samuel	The Weizmann Institute of Science
Dr. Adele Seeff	University of Maryland at College Park
Dr. Herman Skolnick	Hercules Inc.
Prof. Tamar Y. Susskind	Oakland Community College
Dr. James Zigerell	Instructional Television Consortium, American Association of Community and Junior Colleges

Finally , we thank our families for support and understanding as we worked against formidable deadlines.

Gilbert Castellan

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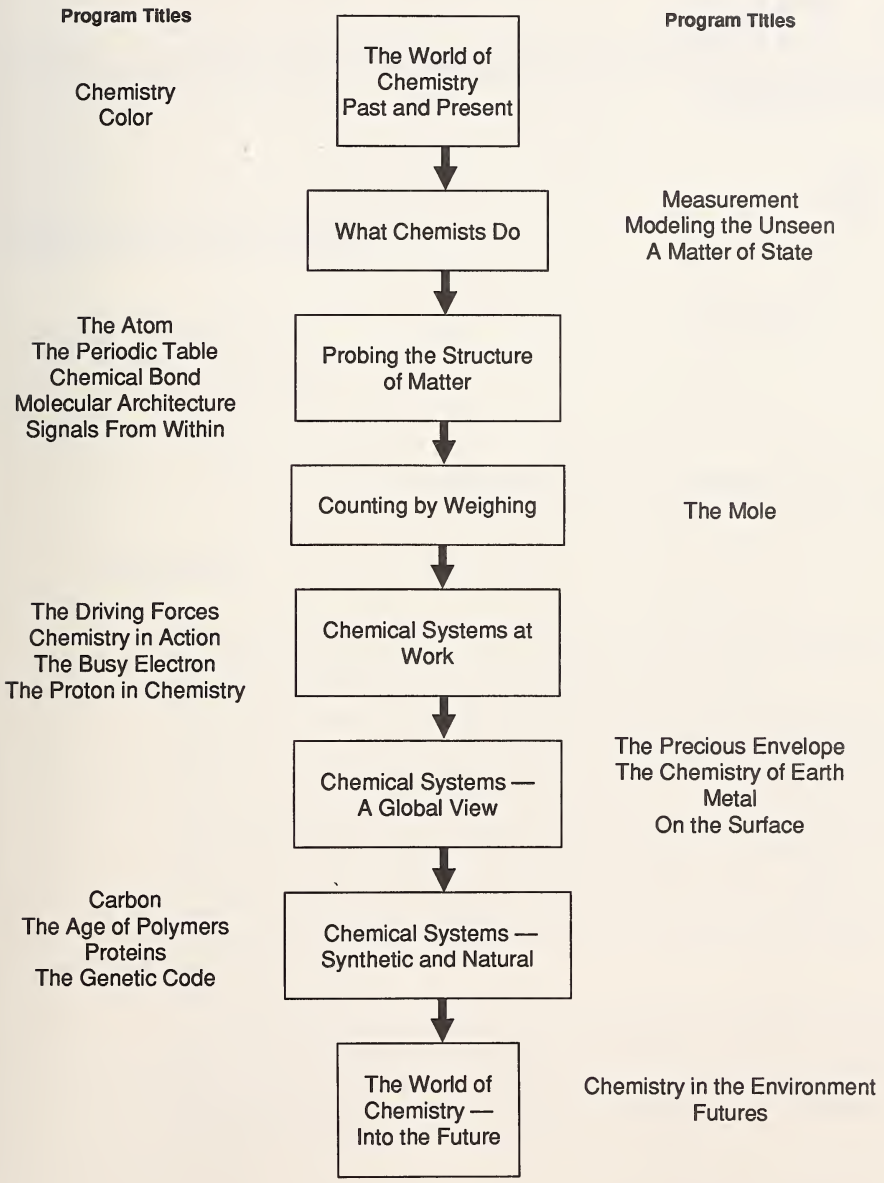
The General Scheme



UNIT 1

CHEMISTRY

BEFORE WATCHING

'The time has come,' the Walrus said,
'To talk of many things:
Of shoes— and ships— and sealing wax—
Of cabbages— and kings—
And why the sea is boiling hot—
And whether pigs have wings.'

— Through the Looking Glass, and What Alice Found There
Lewis Carroll

OVERVIEW

This program is a broadbrush view of the myriad ways that chemistry is interwoven with our society. We look at two facets: first, chemistry as a way to make things, and secondly, chemistry as a way to understand the world around us.

When we look around, we realize that a large proportion of the materials that we deal with every day did not exist a century ago. Something as familiar as structural steel came into use just about 100 years ago. The Eiffel Tower was the first major construction using steel. In the U.S., the National Bureau of Standards came into existence to develope and set standards for the steel to be used in the boilers of steam engines. These boilers exploded with frightening frequency. Steel making was a chemical art; it is now a chemical science. Celluloid, the first 'plastic', had just been invented. Today literally hundreds of plastics make our lives safer and more pleasant. Today pharmaceuticals can be designed to be effective against particular diseases. The list goes on and on.

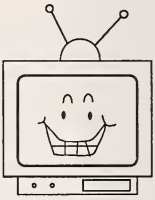
All these things did not just come to be. Behind them all are stories of invention and discovery. We present the Pacemaker and its dependence on the lithium battery, the development of medicines, food chemistry, and personal products as examples to illustrate the broad scope of chemical applications. The program ranges from the serious dream of Nathaniel Wyeth of endlessly recycling plastics to the delight of a young lady who has just had her disulfide bonds rearranged.

Most of these marvelous chemical products would not be available if it were not for chemistry done on a huge scale, that is, chemical industry. The economic impact of the chemical industry is enormous because of the size of the infrastructure needed. This infrastructure includes everyone from the construction and operational people to suppliers of raw materials and the marketers of the products.

The other side of the chemical story is the story of discovery and its contribution to our understanding of the world. Curiosity is the first step on the road to discovery. We have to wonder why. In the program we see chemists who wonder if there are molecular precursors of living material in a meteorite, others wonder about the chemical basis of genetics, about protein structure and about what an atom looks like. Our natural world is chemical, and chemists ponder it.

Once the exploration is begun and experiments tell us about how matter behaves on a macroscopic level, we construct models which explain this macroscopic behavior. These models are our vision of the microscopic constitution of matter. From the ancient elements of air, earth, fire and water we have progressed to a model that is made of atoms and molecules. These, in turn, are made of electrons that move in mysterious ways that make the atom look like a puff of cotton, of protons and neutrons that give mass to an atom. Based on this atomic constitution, we can visualize the dynamics of the interactions of atoms and molecules that result in chemical reactions.

The program concludes with a litany of chemical reactions and demonstrations, reminding us that in chemistry no conclusions would ever have been possible without experiments.



WATCH THE PROGRAM

AFTER WATCHING

QUESTIONS

1. *In the program we hear, " Matter is neither created nor destroyed. But in industry we transform it every day." What basic law lies behind these words? State this law and exemplify it.*

2. *"Explanation is directed toward past occurrences, prediction is directed toward future ones." Discuss this quotation in relation to what chemists do.*

3. *To illustrate how difficult it is to separate science from technology, try to categorize each of the following:*

   a. *Research to elucidate the chemical reactions which produce "the ozone hole."*

   b. *The invention of the process of pasteurization for the preservation of food.*

UNIT 2

COLOR

BEFORE WATCHING

YOU ALREADY KNOW

Matter is made up of atoms and molecules.

Mass is conserved in chemical changes.

READ

Chapter 1: "How Is Science Done?"; "How Do Scientists Communicate?"; "Technology and The Industrial Revolution"

OVERVIEW

This program focuses on colored substances for several reasons. Of course, colors are lovely to look at. But the phenomenon of color has been used extensively as part of our techniques for making chemical observations. Color changes signal chemical changes in a system. This use of "color" was very important in the early history of chemistry, but it is even more important now. Today we can observe "color" changes, not only in the visible region of the spectrum but in the other regions as well, using instruments especially designed for that purpose.

Finally, it was through the invention of the synthesis of mauve, a dye, that triggered the development of the modern age of industrial chemistry. This invention was a remarkable example of serendipity. William Henry Perkin was attempting to synthesize quinine when he discovered instead this beautiful dyestuff, mauve. He immediately set out to capitalize on the synthesis by making the dye in commercial quantities. This set off a wave of industrial syntheses of other dyes and pharmaceuticals. Modern chemical industry was born.

WHAT TO LOOK FOR

COLOR

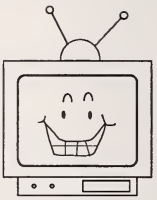
a. sources of colors or dyes
b. dispersion of white light by a prism

COAL TAR AND THE SYNTHESIS OF MAUVE

c. coal tar
d. Perkin and the synthesis of mauve
e. color and molecular structure
f. development of industrial chemistry

INDICATORS

g. swimming pool and the comparison of colors
h. acid-base indicators
i. histological stains
j. clues to DNA structure via color



WATCH THE PROGRAM

AFTER WATCHING

COLOR

a. Sources of colors or dyes

Before the development of the synthetic dye industry in the last part of the nineteenth century, colored materials such as dyes and pigments were all obtained, more or less circuitously, from natural sources.

Pigments are colored solids; examples include vermilion, also called cinnabar, a brilliant red solid, is mercuric sulfide, a compound of mercury and sulfur. Antimony trisulfide, occurs naturally in two forms, both used historically as pigments. One form is orange, the other is black. The black form was used by the Egyptians to paint their eyebrows. Natural lead sulfide, galena, was also used for this purpose.

Dyes are soluble, colored compounds. Well-known natural dyes are alizarin, a red dye extracted from madder root, and indigo, extracted from the leaves of an Indian plant, *indigo fera tinctoria*, as well as the *woad* plant. The extract is colorless; the cloth is immersed in the colorless solution and then hung in the sun. Exposure to air and light chemically transforms the colorless compound to the blue compound, indigo. Indigo is the blue dye used to produce blue jeans. After hundreds of years, it is still the most commonly used dye. After a commercial synthesis was devised in the 1890s and it was produced industrially, the market for the natural material collapsed, causing great hardship for the Indian and other indigo farmers. Tyrian purple, also known as "royal purple", was highly prized as a dye by ancient kings and emperors. Originally obtained from a snail, today we know that Tyrian purple is a bromine derivative of indigo.

b. Dispersion of white light by a prism

Newton's discovery of the dispersion of white light into its component colors by a prism marks the beginning of our understanding of color. This band of colors produced by the prism is called a **spectrum;** in particular it is the visible spectrum of the light falling on the prism. Ultimately, it was established that light is a wave motion and that different colors of light correspond to different wavelengths. The wavelength is the distance between two successive crests (or troughs) of the wave. Violet light is at the short wavelength end of the visible spectrum; it has a wavelength in the region of 400 nanometres (nm). (A nanometre, abbreviated nm,

is one-billionth of a metre.) Red light, at the other end of the visible spectrum, has a wavelength in the region of 800 nm. The visible spectrum is imbedded in a continuum of possible wavelengths of light. The eye is not capable of detecting these other wavelengths; instruments specifically designed for the particular wavelength regions must be used. [You will get acquainted with this kind of instrument in Program 10, "Signals from Within".] Wavelengths less than 400 nm cover the ultraviolet region, the x-ray region, and the gamma ray region, in order of decreasing wavelength. Wavelengths greater than about 800 nm cover the infrared region, the microwave region, and the radio region, in order of increasing wavelength.

The energy carried by a light beam of a given intensity is inversely proportional to its wavelength. Thus, a beam of red light carries less energy than a beam of violet light of the same intensity. We can see visible light simply because the energies associated with the wavelengths in this region are in the range of energies involved in the chemical reactions that produce vision.

COAL TAR AND THE SYNTHESIS OF MAUVE

c. Coal tar

If coal is heated in the absence of air, a mixture of gases is driven off, leaving a solid residue of coke. The coke is used in winning iron from iron ore. Upon cooling, a portion of the hot gases condenses to form a tarry liquid, coal tar. The remaining gas mixture, after passage through water to remove the ammonia, consists mainly of carbon monoxide, methane, and hydrogen. In the 1800s this gas, coal gas, was widely used as a fuel and for illumination. Impurities in the gas caused it to burn with a luminous flame. So, the gas and the solid had important uses, but the coal tar had few. Large amounts of coal tar accumulated as a waste product. By the mid-nineteenth century it was a serious problem. By that time, chemists had succeeded in separating many compounds from coal tar, but none of these compounds had wide use.

d. Perkin and the synthesis of mauve

In 1856 William Henry Perkin was an eighteen year old student at the Royal College in London. He had an idea that he could synthesize the anti-malarial drug, quinine, by oxidizing a mixture of toluidine, a chemical obtained from coal tar, and allyl chloride. In the light of our present knowledge, his reasoning was naive to the point of being ludicrous, but he used what knowledge was available at that time. The experiment failed; he simply got a mess. Later he substituted aniline, another chemical obtained from coal tar, for the toluidine. Again, he got a mess. When he tried to clean the flask with alcohol a purple solution was produced. As it turned out, the purple material could be used as a dye, later called **mauve or mauvein**.

Much to the distress of his chemistry professor, Perkin quit school and began the manufacture of dyes, an occupation from which he retired some eighteen years later as a wealthy man. As far as quinine is concerned, the complete synthesis was first achieved by Woodward and Doering in 1944, 88 years after Perkin's attempt.

One of the most important points of this story is that aniline is a compound obtained indirectly from coal tar. Immediately following Perkin's experience, people began to view coal tar not as a nuisance but as a possible source of useful starting materials for the synthesis of valuable commodities such as dyes and pharmaceuticals. Coal tar remained as an important chemical resource until the 1930s when it was largely replaced by petroleum. Today coal tar has relatively little importance as a source of chemicals.

e. Color and molecular structure

If a substance is to exhibit color, then it must absorb light in some region of the visible spectrum. Suppose we hold a sample of the substance (in a transparent container) in a beam of white light and look at the light that is transmitted through the substance. Suppose that wavelengths in the red, yellow, and green regions of the spectrum are absorbed. The wavelengths absorbed are subtracted from the beam of white light and the wavelengths in the blue and violet region are transmitted. The transmitted light thus appears purple.

Whether or not a compound absorbs in the visible region of the spectrum depends on the arrangement of the atoms in the molecule, that is, upon the structure of the molecule. A very large proportion of dyes have two or more hexagonal rings of carbon atoms (so-called benzene rings) in their molecules. When the connections between these rings require that the rings lie in the same plane, the substance is usually colored. In the program you will have noticed that the mauve molecule had several hexagonal rings and that the molecule was flat; the rings all lay in the same plane. Similarly, the three rings in the phenolphthalein molecule lie in the same plane in the colored form of the dye, while in the colorless form two of the rings are twisted out of the plane. In many of these dyes, the conversion between forms having different colors can be effected by the addition of acid or alkali.

f. Development of industrial chemistry

Before the nineteenth century, the chemical industry in the sense we know it today did not exist. The production of metals from their ores, the production of gunpowder, and the extraction of useful materials from plants, were as close as one could come to the "industrial" side of chemistry; but these were, as often as not, cottage industries. The rise of industrial chemistry in the nineteenth century in Germany, and its success there, depended on the willingness of the industries and the government to invest money in the education of chemists and in basic research and then to wait patiently for results that might be financially rewarding. By 1900, these policies had paid off very handsomely; a wealth of new products, especially dyes and pharmaceuticals, were being produced and sold. In other countries, where

the industrialists insisted that chemists produce practical results immediately, the chemical industry stagnated. By the onset of World War I, in Great Britain, France, and the U.S.A. an almost nonexistent chemical industry was faced with all the demands a wartime economy imposes. Everything had to be done from scratch. The Allies were fortunate that by the war's end they were able to produce the needed materials. A bad experience is a good teacher; in the years following World War I the development of strong chemical industries was encouraged in many countries.

INDICATORS

g. The swimming pool and the comparison of colors

In the program, there is a sequence that shows a lifeguard at a swimming pool taking a sample of pool water, adding a bit of a dye to it in a test tube, then comparing the color of the solution in the test tube with the color of solutions in several other test tubes fastened in a plastic block. The solutions in the block have been made up with different known amounts of acid and, of course, a bit of the dye has been added to each. The dye, called an indicator or an indicator dye, takes on a color characteristic of the acidity of the solution. Thus, when the lifeguard finds the test tube in the block that matches the color in the tube he has prepared from the pool water, he knows that the acidity is the same. From the label on the block he reads the concentration of the acid.

This very simple method, requiring no experience to use, is nonetheless quite effective and is accurate enough for the management of the swimming pool, as well as for many other purposes. With a little refinement this method can be extremely accurate; indicators have been used for accurate chemical analysis for over a century.

h. Acid-base indicators

In the program, Don Showalter does a classic demonstration of the change in color of dye solution upon the addition of acid. The dry ice dissolves in water to produce carbonic acid. As time goes on, more and more dry ice dissolves, and the concentration of the acid increases. In the first tube, the indicator changes from one color to another; in the second tube, the indicator changes from magenta to a colorless form (this is the phenolphthalein described above); in both these cases, the structure of the material changes, and this change is accompanied by a change in color. In the third tube, there are several dyes that change color at different acidities. From this experiment, you can understand how one can make the set of comparison solutions that the lifeguard uses in determining the acidity of the pool water.

i. Histological stains

Another long-established use for dyes is in the staining of tissue for microscopic examination. It was noticed rather early that dyes could be used to enhance the contrast between different structures within cells, between different cells, and between micro-organisms. These effects inspired Paul Ehrlich to attempt to find dyes that would attach only to bacteria. His hope was to modify the dye in such a way as to make it lethal to the bacterium but harmless to the host, thus making it a cure for the disease caused by the bacterium. In the course of his work, Ehrlich designed drugs effective against sleeping sickness and (in 1909) syphilis. In spite of this success, very few other specific drugs were developed between 1910 and 1930. In the 1930s the discovery of the sulfa drugs and penicillin pointed chemotherapeutics in totally different directions.

j. Clues to DNA structure via color

Dyes allowed early scientists to see and identify subcellular structures such as nuclei and chromosomes. Ultimately we began to understand the function of these subcellular structures. We might view Jacqueline Barton's work as being similar but on a molecular level.

In this example, a propeller-shaped dye molecule is allowed to attach itself to a DNA molecule--the molecule that stores the genetic information for an organism. The characteristics of the fluorescence of the propeller molecule are changed when it attaches to the DNA. Again, this is because of a change in structure, albeit in this case a much more subtle change than in the case of indicator dyes. From the ways in which the dye molecule and the DNA molecule might attach to one another, the effect on the fluorescence can be estimated and conclusions about structural features of the DNA can be inferred.

HANDS ON:

1. *Remove a bit of the peel from a radish, the purple part of a turnip, an apple, a beet, or take a piece of red cabbage. Add a drop of vinegar (an acid) to each sample, and add a drop of household ammonia or soap solution (alkaline materials) to another sample. Try the same thing with any other colored foods or flower petals. What do you observe? Tabulate your observations. Try to explain the observations.*

2. *Cut a strip of paper from a coffee filter (or a paper towel if a coffee filter is not available) 2 cm wide and 10 cm long. Draw a line across the strip 1 cm from*

one end. Touch the middle of the line with the tip of a felt-tip pen with black ink. Unbend a paper clip and put it across the top of a water glass. Hang the strip of paper over the paper clip and add sufficient water to the glass so that the tip of the strip nearest the spot of ink is just touching the surface of the water. Observe the strip after a few minutes and after several hours.

QUESTIONS

1. *What is the range of wavelengths (in nm) of visible light?*

2. *If the intensities of the beams are the same, which light beam carries the higher energy, a beam of red light or a beam of violet light?*

3. *How is coal tar produced?*

4. *Why was industrial chemistry in the nineteenth century so successful in Germany but not in other countries?*

5. *What happens to a dye molecule that causes it to change color?*

UNIT 3

MEASUREMENT: THE FOUNDATION OF CHEMISTRY

BEFORE WATCHING

YOU ALREADY KNOW

Mass is conserved in chemical reactions.

The color of light is determined by its wavelength.

The acidity of pool water can be determined by comparing colors.

What is meant by the properties of a substance.

READ:

Chapter 2: "Standards and Measurement"; "Accuracy and Precision"

OVERVIEW

Measurement is a basic means of communication. The need for quantitative specification of things arose very early in the history of mankind. Numbers were invented so that man could count the number of sheep that he owned. The earliest applications of geometry were to land measure ; it was necessary to know how much land belonged to this person or that. In very ancient times, there were measures for wheat, for flour, for wine, and for oil. There were injunctions against false dealing; in the Bible we find,

> "Divers weights and divers measures, both are an abomination to the Lord."

Many of the ancient Sumerian clay tablets with cuneiform writing deal with inventories of warehouses and transactions between merchants involving weights of commodities and numbers of animals.

The origin of the balance, for comparing masses, is lost in antiquity. This measurement device is pictured in ancient Egyptian drawings. The Balance, Libra,

is one of the signs of the zodiac, again of ancient origin. Incidentally, the abbreviation for the pound, lb, comes from *libra*.

The need for standards was recognized early. It was clear that it did not matter what was chosen as a unit of length as long as everyone agreed to use the same one. As long as communities were small and isolated, each little group could have its own units of measure and life could go on. When trade between groups became common then having different systems of measure was a problem. In spite of this, it was not until the end of the eighteenth century that a system, the "metric" system, was devised that was simple enough to make it attractive to many different societies.

This program deals with measurements, particularly those of interest to chemists and scientists generally. Accurate measurement is a necessity in science; without it we cannot communicate. We have included some information on standards and some applications to chemical analysis.

WHAT TO LOOK FOR

UNITS

a. mass of antacid tablet

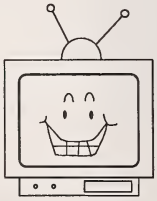
STANDARDS

b. need for standards
c. agreement on standards
d. variety of standards

APPLICATIONS

e. concentration of a solution
f. analysis for salinity in sea water
g. spectrophotometry
h. calibration curve
i. precision and accuracy
j. fluoride and cavities

WATCH THE PROGRAM



AFTER WATCHING

UNITS

a. mass of an antacid tablet

The mass of the antacid tablet is an example of a **measurable property.** A measurable property is any property to which we can attach a number after comparison with a standard. After the first weighing, we attached a number, 1.1, to the mass of the tablet. Clearly, the number, 1.1, by itself is meaningless. It could be 1.1 tons, or 1.1 pounds, or 1.1 ounces, or 1.1 kilograms, or 1.1 grams, or whatever. The number only has meaning if a unit is attached to it. The tablet has a mass of 1.1 grams. Similarly, any measurable property must be expressed by writing a number multiplied by a unit; for example:

Mass of the tablet	= 1.1 x 1 gram
Circumference of the earth	= 40,000,000 x 1 metre
Average length of a day	= 86,400 x 1 second

These units have standard abbreviations, fixed by international agreement, so that the properties above would usually be written:

Mass of the tablet	= 1.1 g
Circumference of the earth	= 40,000,000 m
Average length of a day	= 86,400 s

It is understood that the abbreviation contains the idea of multiplication by the unit.

Note on mass and weight: The mass of any object is a measure of the amount of matter in the object, while the weight is a measure of the force acting on the object as a consequence of a gravity field. Thus, a given object has the same mass on the earth as on the moon but has quite different weights. Having said all that, from now on we will use the terms "mass" and "weight" interchangeably.

Traditionally (for at least two centuries), the process by which we measure the mass of an object has been called "weighing". There has been a recent move to try to rename this process and call it "massing", as if we had only noticed the difference between weight and mass five years ago; it seems excessively pedantic to change the name at this late stage of the game.

STANDARDS

b. need for standards

The numbers obtained above have, in each case, been obtained by some method which compares the property in question with a standard for that property. This method may be direct or indirect. For example, if we measure the mass of the tablet using a two-pan balance, the comparison is direct. The tablet is put on one pan and the standard masses on the other. The number and kinds of standard masses are substituted until the pans are balanced. In the single-pan analytical balance used in the program, the standard masses are hidden inside the balance and are substituted by turning the knobs on the outside. Again, the mass of the tablet and the standard masses are directly compared. To measure the length of a desktop, we would most likely use a measuring tape that is marked with units and subdivisions; the measuring tape is our standard, and the comparison is direct. To measure the circumference of the earth requires an indirect astronomical method; obviously, we are not going to girdle the earth with a measuring tape.

c. agreement on standards and measurement system

For any of this to be practical, there must be general agreement as to what a "gram" is, and what a "metre" is. That is, there must be standards and there must be laws to enforce the use of these standards. All of this did not come easily. In the 1790s in France, a new set of standards of measure was developed. Along with these standards was the convention that only decimal multiples and submultiples of the units would be recognized. This measurement system came to be known as the "metric system". The modern implementation of this system is called The International System of Units, abbreviated SI from the French, Le Systeme International d'Unites. Today the SI is truly international; it is in everyday use in every country in the world but three: the United States, Burma, and Liberia. Ironically, the only legal definition of the "inch" as well as other units of measure in the United States is in terms of their metric equivalents, and this has been true for over a century. Unfortunately, it leaves the United States with cumbersome and archaic units of measure in daily use.

The decimal multiples and submultiples of the base units are indicated by a prefix attached to the name of the unit. For example, the prefix, kilo, multiplies the unit by 1000. Just as the names of the units are abbreviated, the prefixes also have standard abbreviations. The letter, k, is the abbreviation for kilo. Thus:

1 kilometre = 1 km = 1000 m
1 kilogram = 1 kg = 1000 g

Similarly, the prefix, deci, multiplies the unit by one-tenth:

1 decimetre = 1 dm = 0.1 m

The prefix, centi, multiplies by one-hundredth:

1 centimetre = 1 cm = 0.01 m

The prefix, milli, multiplies by one-thousandth:

1 millimetre = 1 mm = 0.001 m

A complete list of prefixes is found in the Appendix to the text.

The advantage to this method of prefixing is that we can choose the unit suited to the task. Thus, to measure the distance between two cities, we would use the kilometre. To measure the circumference of the earth, we could use the kilometre or the megametre:

1 megametre = 1 Mm = 1,000,000 m

The earth's circumference could be expressed as 40,000 km, or 40 Mm. Thus, to go from one unit to another requires only that we move the decimal point. Contrast this with the English units:

1 ft = 12 in; 1 yd = 3 ft; 1 rod = 16 ft; 1 mi = 5280 ft

A non-trivial calculation is involved in each step of converting from one unit to another.

To measure very tiny things, such as atoms, we would use the picometre; the prefix, pico, multiplies by one-millionth of one-millionth.

1 picomètre = 1 pm = 0.000000000001 m

Atoms are of the order of a hundred picometres in diameter. The radius of the mercury atom is about

300 picometres = 300 pm

Even more importantly, the metric units form a system. This in contrast to the English units, which are not systematic. In the SI, once the base unit of length, the metre, is defined, then the base unit of area is the square metre, and the base unit of volume is the cubic metre. The cubic metre is rather large for household measurements of volume, e.g., for milk, or wine, or gasoline. So for these, we use

one-thousandth of a cubic metre; this is the litre, 1 L = 0.001 m^3. Contrast this with the English units; the common units for volume are the gallon or the quart. What relation to the cubic inch? 1 gallon = 231 in^3 and 1 quart = 57.75 in^3

Physical embodiments of the standards are kept in many places throughout the world. The prototype metre, a platinum-iridium bar with two parallel lines engraved upon it, was constructed in the 1790s. The distance between the two engraved marks is one ten-millionth of the length of the earth's quadrant as it was established at that time. The earth's quadrant is the distance between the North Pole and the equator.

A cylindrical piece of platinum-iridium alloy was constructed equal in mass to the mass of one cubic decimetre of water at the temperature of its maximum density. This cylinder of metal is the prototype kilogram.

These prototypes, as well as prototypes of other standards, are kept at the International Bureau of Weights and Measures in Paris. Once these prototypes existed, copies of them were made and distributed throughout the world. In the U.S.A., the National Bureau of Standards has copy number 27 of the metre and copy number 20 of the kilogram. For a nominal fee, the Bureau will calibrate a set of masses in terms of the Bureau's standard set for anyone who has need of this service.

As time passed, the science of measurement, metrology, advanced. Today, the prototype metre is no longer the standard of length; the space between the two engraved marks does not define a length with sufficient accuracy. Today the metre is defined by the length of the path traveled by a light beam in a vacuum in 1/299792458 second. This replaces a length measurement by a time measurement, which today can be done with much greater accuracy.

d. variety of standards

We have mentioned standards for length and mass. But there are standards for any kind of measurement that we can think of making. The National Bureau of Standards can provide standards of mass, of length, of chemical composition (hundreds of samples), of melting points for the calibration of thermometers, and, very recently, a standard sample of microspheres manufactured in space so that the spheres would be as nearly spherical as possible. These are only a few examples. The standard diet illustrated in the program is another. All of these have important applications in laboratory work and in manufacturing.

APPLICATIONS

e. concentration of a solution

Chemical reactions between solid substances often take place more rapidly if the solids are dissolved in a suitable solvent; water is one of the common solvents used. One of the very useful things about solutions is that the amount of a dissolved substance in a given amount of solvent can often be varied over a rather wide range. Dissolving the substance in a solvent also makes it possible to easily measure the amount of substance by measuring the volume of the solution.

For example, suppose that we wish to add 0.02 grams of a substance to another substance that will react with it. It is not usually convenient or even practical to weigh so small a mass as 0.02 g of material directly. Instead, what I can do is weigh out 1.00 g of the substance, dissolve it in water, and adjust the volume of the solution to 100.0 millilitres.

1 millilitre = 0.001 litre

Then, in every millilitre of the solution there is 0.0100 g of the dissolved solid. We can easily add 0.02 g to our reaction mixture by adding 2 mL of the solution. The volume measurement is easily done using a burette; a burette is a straight glass tube of uniform cross-section, closed at the bottom by a valve (called a stopcock) which can be opened to allow the liquid in the burette to flow out. The tube is graduated with a set of lines that mark the tube in millilitres (the major divisions) and in tenths of millilitres (fine subdivisions). Thus, by operating the valve and allowing the level of the liquid to fall by two major divisions, we will have delivered two millilitres of the solution into the container below the burette.

f. analysis for salinity in sea water

The application of volumetric measurements to the determination of salinity in seawater is shown in the program. In this demonstration, Don Showalter prepares a "standard solution" of silver nitrate in distilled water by dissolving 1.00 g of silver nitrate in 100.0 mL of water in a volumetric flask. This is called a standard solution because it contains an accurately measured quantity of silver nitrate in an accurately measured volume of solution. He next places an accurately measured volume of seawater in a small flask. Also placed in this flask is a small amount of an indicator substance, usually a dye; this substance is selected so that when we have added just enough silver nitrate to react with the chloride in the seawater, the indicator will change color. By measuring the volume of the silver nitrate solution delivered from the burette to produce the color change, we can calculate how much silver nitrate was used. From this and a knowledge of the chemical reaction we can calculate how much chloride is present and thus we obtain the salinity of the sample. This is a classic example of the volumetric analysis (analysis by measuring volumes) for chloride.

g. spectrophotometry

When it is necessary to measure very small amounts of a substance, it is often possible to use a technique called spectrophotometry. In this technique, a beam of light of a selected wavelength (in other words, a certain color) is passed through a solution containing the substance. The intensity of the beam after it emerges from the solution is compared with the intensity of the beam that emerges from a 'blank' solution. A 'blank' solution is the same as the test solution in every way except that it does not contain the substance to be determined. The substance absorbs the light, so the decrease in the intensity is a measure of the amount of the substance present.

The spectrophotometric method is practical for measuring the concentration of metal compounds because of the very deeply colored substances that can be produced by the addition of special reagents to solutions containing metal compounds. Because of the intensity of the colors produced, even in very dilute solutions it is possible to measure a significant absorption of the beam.

h. calibration curve

From a measurement of the decrease in intensity of the beam a quantity called the "absorbance" can be calculated. Measurements are made on several solutions having different known concentrations of the colored substance. The absorbance of these solutions is plotted against their concentrations, and a smooth curve is drawn through the points. This curve is called a "calibration curve". Once we have constructed such a calibration curve, we measure the absorbance of a solution in which the concentration of the metal compound is not known. We move along the curve until we reach the value of the absorbance of the solution; from this point on the curve we can read the corresponding value of the concentration of the metal compound in the solution.

i. precision and accuracy

"Measure twice; cut once."

—a carpenter's motto

It is always necessary to repeat a measurement a few times to be sure that there is at least some consistency in the method. Suppose we made three measurements of the salinity of a sample of sea water and found values of 6%, 15%, and 33% sodium chloride by weight. From these numbers, we would have to conclude that something was seriously wrong, either with our method or with the way it was being implemented. On the other hand, if we had made only one measurement, we might well have concluded that 6% was the correct value.

Even in a simple analytical procedure there are perhaps a dozen distinct operations; each of these operations yields a slightly different result when it is repeated. As a consequence, the repetition of an analysis yields a slightly different numerical result. To estimate the reproducibility of the method, we must repeat the analysis

several times. In routine work the rule is: repeat at least twice, preferably three times. The table below shows the values obtained by an analyst for the percent of sodium chloride in a mixture.

% sodium chloride		deviation
12.23		+ 0.07
12.11		− 0.05
12.14		− 0.02
average = 12.16	average =	0.00

The average of the three values is 12.16%. We need some measure of the scatter of the individual measurements around the average value, so we calculate the amount by which each value deviates from the average:

deviation = measured value minus average value

Example: deviation = 12.2 − 12.16 = 0.07 (first entry under "deviation")

When we add the deviations, both positive and negative, we get a zero and, hence, a zero average deviation. The definition of the average value requires that result. If, instead of adding the deviations algebraically, we add their absolute values (that is, we ignore the negative signs) we can obtain a measure of the scatter. Thus:

$$(0.07 + 0.05 + 0.02)/3 = 0.14/3 = 0.047 = 0.05$$

The average distance of the measured points from the average value is 0.05. This value, 0.05, is a measure of the **precision** of the measurements. The value would usually be reported as

12.16 ± 0.05 % sodium chloride

Since the average scatter is relatively small compared to the value itself, we regard this as a reasonably precise method. When the procedure is repeated, the results will be in good agreement.

By itself, this does not give us any idea of how close the number 12.16 is to the true value of the percent of salt in the sample. It only tells us that if we use this particular method to analyze the mixture, the values we get will cluster near the value 12.16.

Before we can accept the number 12.16 as being close to the true value, we must have done many analyses of many salt samples using several different methods, including this method. If they all agree, then we can begin to believe that 12.16 is close to the true value. It is only by constantly questioning and cross-checking various methods for consistency that we can finally establish how close the 12.16 is to the true value. Once it is established that the method produces a value near the true value, we can evaluate the **accuracy** of the method. The **accuracy** takes into

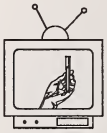
account not only the precision of the measurement but also any intrinsic biases that are introduced by the method itself. For example, experience may have shown that because of a systematic bias this method always produces a result that is 3% high. Then, we would reduce the 12.16 by 3% (.03 x 12.16 = 0.37) and obtain 12.16 – 0.37 = 11.79. The true value would then be taken as 11.79, with the same precision as before.

In brief, the precision of a value is a measure of how closely measurements of the value agree. The accuracy of a value is a measure of how close the value is to the true value of the quantity.

j. fluoride and cavities

The story about fluoride in drinking water and tooth cavities illustrates the importance of being able to make accurate measurements at extremely low levels of concentration.

HANDS ON



1. *Units of measure are a means of communication. What things do you measure every day in your car, in the kitchen, in your bathroom, in your workplace, and in your living room? Make a list of the units used.*

QUESTIONS

1. *How do you know that the scale over the vegetable counter at the grocery store is accurate? Or that the pump at the gasoline station measures the volume accurately?*

2. *What is meant by the precision of a set of measurements?*

3. *What is meant by the accuracy of a set of measurements?*

4. *What is the measuring device that many people, regardless of their occupation, carry everywhere all day and all night?*

UNIT 4

MODELING THE UNSEEN

BEFORE WATCHING

YOU ALREADY KNOW

The microscopic particles of matter have mass.

Light is modelled as a wave motion.

READ

Chapter 3: "The Greek Influence"; "Dalton's Atomic Theory"

OVERVIEW

This program presents several examples of how scientists try to comprehend the physical world. At the heart of this endeavor is observation of the system in question. Our first observations of any system are macroscopic ones. As time went on, our experimental methods became more sophisticated, and we could observe more subtle types of behavior.

Once having made the observations, we are driven to interpret them in terms of things already familiar to us. We believe that they are intelligible in terms of some combination of behaviors of systems that we already understand. So, our task is to put together the right combination of systems; in brief, we build a mental model of the system. We make the model of familiar things; little balls for the atoms, springs for the forces holding the atoms together, etc. We endow the model with familiar properties; the balls have mass, they may be hard or soft, the springs may be stiff or flexible. Then, by applying the laws of mechanics to the model, we ask whether this model can predict the behavior that we observe in the system. As we learn more about the system and the model, we tinker with the model, we change it, we refine it, we even go so far as to change the laws of mechanics to bring the model to where it will predict correctly the properties of the system. As the model is improved, we

often gain new understanding about the old familiar systems from which the model is built.

As you watch the program notice particularly that the models are basically simple. We try not to clutter them with more complications than are necessary.

WHAT TO LOOK FOR

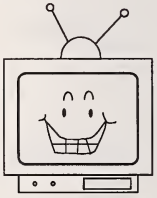
MODELS IN MACROSCOPIC SYSTEMS

a. sculpture
b. locked boxes
c. Io

MODELS IN MICROSCOPIC SYSTEMS

d. kinetic molecular model for gases
e. models of single molecules; lock and key example

WATCH THE PROGRAM



AFTER WATCHING

MODELS IN MACROSCOPIC SYSTEMS

a. Sculpture

A statue of Abraham Lincoln is a representation of the artist's image of Lincoln. The statue is a way for the artist to communicate to others what Abraham Lincoln looked like. The artist has made a model of the form of Abraham Lincoln. This very simple example of a model is nonetheless very similar in concept to the models we construct of physical systems to explain them.

The task of the chemist is more difficult than that of the sculptor of the Lincoln statue. In the attempt to explain the macroscopic behavior of a chemical system, the chemist must construct a model that will represent the unseen and often unknown interior structure of the system in terms of things that are familiar.

There is a classic story about the little boy who was busily drawing a picture. His mother asked, "Johnny, what are you doing?"

> "I'm drawing a picture of God," he responded.
>
> "But Johnny," she exclaimed. "Nobody has ever seen God. Nobody knows what God looks like."
>
> "They will when I get finished," he replied.

Johnny was a chemist.

b. The locked box

The episode in the program that involves the locked boxes is a neat and simple example of how our minds almost force us to build a mental image, a model, that will explain the observations that we make in terms of familiar things.

The one box makes a satisfying rattling sound when shaken; it is heavy; and there is plenty of room for the heavy objects to move around inside the box. One of the children immediately says that it is full of change (coins). The x-ray photo supports the idea that it is full of chunks of metal. Finally, opening the box and looking at the contents verifies the model.

The second box is unexpectedly difficult. It doesn't rattle; there is no evident shift in weight when it is shaken; it is very light. Everyone agrees that the box is empty. The x-ray photo shows nothing and thus supports the (false) view that the box is

empty. Opening the box shows that it is full of cotton balls. Once we know the result it is easy to construct a logical chain of thought that would have prevented us from eliminating the possibility that the box contained an immobile mass of very light material that was transparent to x-rays. But the simplest supposition was that the box was empty. And, in the absence of contradictory evidence, that was probably the most reasonable supposition. But the example of the cotton balls will always remind us to keep an open mind and to constantly check new evidence against the predictions of the model.

Keep in mind that when we, as chemists, construct a model of a chemical system, it is not possible to "open the box" to confirm the model. We must continue to devise new experiments and thus make new observations on the system. Are these new data consistent with the model? If so, fine; if not, can the model be modified to explain the new data? Does the model predict behavior that has not yet been observed? Can we design an experiment that will prove or disprove this prediction? Only by intensive examination and cross-examination do we finally come to have confidence in the model and understand its limitations.

c. Io

The model of the structure of Io is a beautiful example of how a model can be refined and/or changed entirely upon the aquisition of new evidence. The limited evidence available from classical astronomical observations led to a model of this moon of Jupiter that assumed it was like our own moon. It was cold, but had a crust of a white, salt-like material. But the Voyager I cameras actually photographed a volcanic eruption as it flew by. All bets were off. A new model was needed that could explain where the energy came from to produce the volcanos.

MODELS IN MICROSCOPIC SYSTEMS

All of the models discussed above dealt with examples from the macroscopic world, the world of objects that can, at least in principle, be seen or touched and felt. The chemist, on the other hand, makes observations at the macroscopic level, but attempts to understand those observations in terms of a model of the microscopic structure of matter. Historically, this brought us to the ideas of atoms and molecules. We know now that the size of an atom is of the order of one ten-billionth of a metre. It is in terms of events on this scale that we try to model the observed behavior of our macroscopic systems.

To get some feeling for the smallness of the atom, consider the following: if we were to expand all the atoms in our body until each atom was the size of a golf ball, we could span the distance between the earth and the moon with our outstretched arms.

d. Kinetic molecular model for gases

The observations on the properties of gases that we wish to interpret in terms of a microscopic model are:

1. A gas exerts a pressure (= the force on a unit of area) on the walls of the vessel confining it.
2. The pressure of the gas changes if we change the volume of the containing vessel. The relation is simple; if we increase the volume, the pressure falls, and vice versa. Specifically, if we double the volume, the pressure drops to one-half its value, and vice versa.
3. If we add gas to a container of fixed volume, the pressure increases. Again the relation is simple: if we double the mass of the gas, the pressure will double.

The assumptions that make up our model of the gas are:

1. The gas is composed of an extremely large number of very small particles. In a pure gas the particles all have the same mass. (Note that the volume occupied by the particles is negligible compared to the volume of the vessel.)
2. The particles are moving very rapidly in all directions. (The motion is chaotic.) The motion obeys Newton's laws.

It turns out that these assumptions are sufficient to interpret the behavior of gases rather well as long as the pressure is not too high.

The fact that the gas exerts a pressure on the walls of the container is accounted for by the collisions of the particles with the walls of the container. Just as a tennis ball exerts a force on a wall when it hits the wall and rebounds, so the particle exerts a tiny force on the wall each time it hits. The pressure is a consequence of the enormous number of impacts of all the particles that collide with the walls in a specified time interval.

The dependence of the pressure on the volume is accounted for by the change in the number of impacts in a given time interval. It can be shown that the pressure depends on the number of impacts in a given time interval. [Suppose that five particles hit the wall in one second. That exerts a certain pressure on the wall. If, instead, the five particles hit in 1000 years the pressure on the wall obviously would be very much less.] Doubling the volume doubles the distance the particle must travel between collisions with the wall. This, in turn, reduces the number of particles hitting in a given time interval by one-half. Thus, the pressure falls to one-half its value.

Clearly, if we double the number of particles in the vessel keeping the volume fixed we will double the number of collisions with the wall in a given time interval; this doubles the pressure.

Thus, we see that a very simple model of the gas can provide a quantitative interpretation of macroscopic gas behavior. But keep in mind that it took generations of scientific debate to arrive at this simple model.

e. Models of single molecules; lock and key example

The atom was originally proposed as the smallest portion into which a substance could be subdivided. Since the time of Dalton, it has been customary to visualize this small particle as a little ball. When two or more atoms came together to form a molecule of a compound substance, the molecule was visualized as a cluster of little balls, possibly of different sizes if different kinds of atoms were involved. Over the years, chemists came to realize that the way the atoms were arranged in the molecule was important. Thus, the models of molecules began to show the geometric shape of the molecule as well as the numbers and kinds of atoms in it.

As long as there were only a few atoms in the molecule, one could easily keep a picture of the molecule in mind. However, when one deals with very large molecules, such as proteins or DNA molecules that contain thousands of atoms, it is very difficult to visualize the details of such a structure. It was usual to make a physical model of complex molecules so the details could be seen. Today, rather than building a model by connecting little wooden balls, we instruct a computer to build a model of the molecule and display the result as a graphic on the computer screen.

The computer graphics picture of a DNA molecule shown in the film has been assembled by specifying to the computer the way each atom is connected to all its neighbors, the distances between neighbors, and the angles between the connections. Different kinds of atoms are shown in different colors. The computer then displays the model of the molecule as a graphic; we can turn it around on the screen, look at it from various angles, and thus gain an understanding of its intricacies that we could not as easily gain in any other way.

If we construct models of molecules that interact with each other, we can gain an understanding of the details of the interaction. For example, some drugs are effective because they interfere with the action of an enzyme. This can happen by the drug fitting like a key into a particular site on the enzyme which acts as the lock. Once this site is occupied by the drug molecule, it is no longer available for its usual function. The shapes of the two molecules play a crucial role in this interaction. These shapes are most easily comprehended using the molecular models generated by a computer.

HANDS ON

1. *Light a candle and watch it burn. Create a model to explain the "disappearance" of the candle. Suggest and perform simple experiments to test your model. Modify the model in the light of these experiments.*

QUESTIONS

1. *Which one of the following generally* **does not** *lead to new scientific discoveries?*

   a. *investigating things that people do not understand*

   b. *observing the effects that one substance has on another*

   c. *preparing one's mind through education*

   d. *believing everything you hear or read about*

2. *Discuss the statement: "Models are not real but exist only in the scientist's mind."*

3. *In a closed system a gas liquefies on cooling. Modify the kinetic molecular model of a gas to predict the existence of the liquid.*

4. *In what way does a chemical system resemble a "black box"?*

5. *J. Willard Gibbs developed some fundamental scientific ideas. He was concerned with interpreting experimental data and with predicting the results of new, as yet undone, experiments. In his work, he used mathematical equations rather than laboratory apparatus. Based on this information, would you regard J. Willard Gibbs as a scientist?*

UNIT 5

A MATTER OF STATE

BEFORE WATCHING

YOU ALREADY KNOW

Matter is made up of atoms and molecules.

The kinetic molecular model for gases.

READ:

Chapter 2: "States of Matter"

Chapter 11: "The Fractionation of Air"

OVERVIEW

The program gives examples of the states of matter, solid, liquid, and gaseous, and contrasts their properties. The properties are interpreted from the standpoint of structure, and from the standpoint of the energy changes involved in the change from one state to another.

The volume of a substance in the liquid state is not much different from that in the solid state. This is because in both the liquid and the solid the volume is essentially the volume of the molecules themselves. In contrast, the volume of the gas is enormously greater, a thousand times or more, than that of the liquid. This is because the volume occupied by a gas is nearly all empty space. This is brought home to us dramatically in the scenes of the tank farm, where natural gas is stored both in the liquid state and in the gaseous state. What interpretation can we give this in terms of the structure of these states of matter? Structurally, a crystalline solid is completely ordered; the arrangement of the constituent particles in the crystal is fixed and regular. If the temperature of the solid is raised, the particles vibrate about their positions with ever increasing amplitude. At the melting point, these vibrations are large enough to tear the particles from their position; energy must be supplied to accomplish this. In the liquid the particles are somewhat free;

they can move from place to place within the liquid even though they are still weakly attached to their neighbors. At the boiling point, sufficient energy must be supplied to free the particles completely from their neighbors. The motions of the gas molecules are chaotic and independent of the presence of the other gas molecules. The kinetic energy of this chaotic motion is called the thermal energy; the thermal energy is a measure of the temperature of the system. The greater the thermal energy the greater is the temperature. This thermal energy produces what may be called a "randomizing force" on the particles of the system. If this randomizing force is sufficiently strong (i.e. if the temperature is high enough) to overcome the attractive forces acting between the particles, then the particles can be torn away from each other; the substance vaporizes.

The program also uses the kinetic molecular model to interpret the pressure-temperature behavior of a gas.

WHAT TO LOOK FOR:

GASES AND THE KINETIC MOLECULAR MODEL

a. the collapsing can
b. the heated sphere
c. the graphic of molecular motion

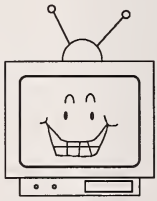
LIQUEFACTION OF GASES

d. the storage of liquefied natural gas (LNG)
e. properties of liquid nitrogen
f. cooling bromine

CRYSTAL

g. the macroscopic appearance of the crystal as a reflection of its microscopic structure.

WATCH THE PROGRAM



AFTER WATCHING

GASES AND THE KINETIC MOLECULAR MODEL

a. The collapsing can

The collapsing can is a dramatic demonstration of the existence of an atmospheric pressure. Boiling the water in the can vaporizes the water; the water vapor drives out the air. When the cap is put on to seal the can, there is no air in the can, only water vapor and liquid water. As the closed can cools, the vapor condenses and the pressure inside the can decreases drastically. The pressure of the atmosphere on the outside crushes the can. There are two effects operating here. One is the simple decrease in pressure resulting from the temperature decrease, a relatively small effect. The second effect is the drastic decrease in pressure produced by the condensation of the water vapor; in this process water molecules are removed from the space occupied by the vapor. If we removed all of them there would be no pressure at all inside the can. Since a few molecules remain in the vapor space even at low temperatures, there is a small pressure inside the can, but not enough to withstand the force exerted by the atmosphere on the outside.

b. The heated sphere

In Program 4 the pressure exerted by the gas was accounted for in terms of the number of collisions made by the particles with the wall in a fixed time interval. The force exerted on the wall depends on the mass of the particle and the speed with which it collides with the wall in addition to the frequency of the collisions. In Program 4 we assumed that the average speed of the particles did not change. That is equivalent to saying that the temperature of the gas is constant. In the demonstration here, we show the effect of increasing the temperature of the gas. Increasing the temperature increases the average kinetic energy of the particles and therefore their average speed. This has two effects; the faster moving particles exert a greater force on the wall when they collide and, because they move more quickly, they collide with the wall more frequently. Both these effects act to increase the pressure of the gas.

c. The graphic of molecular motion

The graphic shows the increase in speed of the gas particles as the temperature is increased. Of course, very few particles are shown very much enlarged.

LIQUEFACTION OF GASES

d. The storage of liquefied gases

The handling of gases on an industrial scale is a problem simply because at pressures near one atmosphere most of the volume occupied by the gas is in fact empty space. Thus, to deal with a large amount of gas the storage tanks must be enormous and to move the gas from here to there requires very large diameter pipes and equipment. The usual industrial solution to this problem is to operate at high pressures, often of the order of several hundred atmospheres. This brings the equipment down to more reasonable size but, of course, it must be able to withstand the high pressures.

The alternative to using high pressures is to convert the gas to a liquid. This is advantageous for storing and transporting large quantities of the material. The method is in everyday use for storage and transport of natural gas (methane), oxygen, nitrogen, and propane. By using enormous pressures, we could reduce the volume of the gas to that of the liquid, but if this "liquid" is to exist at low pressure (around one atmosphere) we must reduce its temperature, and specifically we must reduce its energy by removing the energy of vaporization. This means that the temperature must be reduced to the boiling point of the material. For natural gas this temperature is -161 °C; for oxygen it is -183 °C; for nitrogen -196 °C. If these materials were stored in ordinary containers, heat would flow in quickly, the liquid would vaporize and we would be back where we were before. So, they are stored in double-walled vessels like a Thermos bottle. There is a vacuum in the space between the walls. This reduces the heat conduction to a point where it is tolerable. The white tanks shown in the natural gas tank farm contain liquid natural gas (LNG). Upon demand, the liquid is vaporized and sent to the consumer by pipeline as a gas. The temperature inside one of these tanks is about -161 °C, the boiling point of methane. In recent years, we have been purchasing liquid natural gas from Algeria; it is sent to this country by sea in huge tanker ships.

e. Properties of liquid nitrogen

Oxygen and nitrogen are two other examples of gases that are bought, sold and shipped as liquids in tonnage lots. Everyone has seen pictures of the tank truck of liquid oxygen drawing up to fuel the spacecraft on the launch pad. Similar tank trucks containing liquid nitrogen are common sights on the highways. The temperatures inside these double-walled tanks are the boiling points of the gases. In the case of nitrogen, this temperature is -196 °C.

When an object is immersed in liquid nitrogen, heat is withdrawn from the object and goes to evaporate some of the liquid; hence the noisy boiling when an object is first dropped in the liquid. The mechanical properties of many substances are drastically different at this low temperature from those at ordinary temperatures. The ball, instead of deforming and then returning to its original shape as it would if hit by a hammer at room temperature, is brittle at liquid nitrogen temperature and

shatters when tapped by the hammer. The flower petals, instead of being soft, are stiff and break into bits when the hand closes on them.

Since liquid nitrogen is so very cold it is used for the quick freezing of foods. The water in the foods is chilled so quickly that it does not have time enough to grow ice crystals but simply hardens as a glassy solid. Because ice crystals are not formed, this kind of quick freezing produces minimal damage to the cellular structure of the foodstuff. Much effort has gone into investigating whether donated human organs, such as hearts, or kidneys, or livers, could be quick frozen undamaged and preserved until needed for the replacement of diseased organs. Unfortunately, as the frozen material warms up, ice crystals form and produce much tissue damage. Work to solve this problem continues. Proposals have even been made to quick-freeze people suffering from incurable diseases, the hope being to revive them sometime in the indefinite future when, presumably, a cure will have been developed.

f. Cooling bromine

When the tip of the container of bromine is immersed in liquid nitrogen, the red liquid bromine freezes to a yellow solid; simultaneously, the condensation of the gaseous bromine to form liquid reduces the number of bromine molecules in the gas, so we observe a decrease in intensity of the red color in the glass balloon. Finally we have the yellow solid in the bottom of the container, the red liquid near where the surface of the liquid nitrogen was, and a relatively pale red color in the gaseous region.

Density

An important property of any sample of matter is its density. To compare the densities of different materials, think of a fixed volume, such as one cubic metre. Imagine that volume being filled with different materials and weighing the material in it. The masses obtained in this way are the numerical values of the densities of the materials. The numbers would look like this: if the unit of mass is the metric ton = 1 tonne, then the unit of density is "tonne per cubic metre"; abbreviated tonne/m^3. (Note: These same numbers express the densities in gram/cubic centimetre.) The values for liquids and solids in the table are for temperatures in the range 18–25 ^{o}C.

	Substance	Density tonne/m^3	Substance	Density tonne/m^3
Solids	Ice	0.80	Glass	2.4-2.8
	Paraffin	0.87 - 0.91	Granite	2.6-2.8
	Wood, balsa	0.11 - 0.14	Quartz	2.65
	Wood, white pine	0.35 - 0.50	Aluminum	2.70
	Wood, oak	0.60 - 0.90	Iron	7.9
	Sugar	1.59	Copper	8.9
	Salt (NaCl)	2.18	Silver	10.5
			Lead	11.3
			Gold	19.3
Liquids	Ether	0.736	Water	1.0
	Alcohol	0.791	Chloroform	1.49
	Gasoline	0.60-0.69	Sulfuric acid	1.83
	Olive oil	0.92	Bromine	3.12
Gases (25 °C, 1 atm)	Hydrogen	0.0000818	Nitrogen	0.00114
	Helium	0.000164	Oxygen	0.00131
	Methane	0.000654	CO_2	0.00180
	Water vapor	0.000735	Cl_2	0.00290

We see from the values in the table that solids are relatively dense. The mass of a cubic metre of ordinary stone (granite or quartz) would be between 2.6 and 2.8 tonnes. A cubic metre of liquid water has a mass of only 1.0 tonne. The reason a stone sinks in water is because its density is higher than that of liquid water. Substances with densities less than that of water float on water. The densities of solids range from 0.11 tonne/m^3, (balsa wood) to 22.5 tonne/m^3 (osmium). Osmium has the highest density of any material known. Lead, at 11.3 tonne/m^3, is in the middle of that range. Gold, at 19.3 tonne/m^3, and platinum, at 21.4 tonne/m^3, are also extremely dense. This fact should be borne in mind if you are planning to pick up and run off with a piece of any size. For example, characters in adventure-type B movies are constantly picking up and running down the hall with "solid gold" statues; statues which by any reasonable estimate would weigh several tonnes.

The densities of liquids are comparable to those of the solid from which they are derived. Usually the liquids are slightly less dense than the solids, perhaps by as much as 10%. This happens because the structure usually expands a bit when the solid melts. There are some exceptions to this, the most outstanding one being water. Liquid water is about 10% more dense than ice. This is because ice has a crystal structure that is very open; it has large holes in it. When ice melts the structure collapses, the water molecules (which can move in the liquid) move to fill in the holes. The result is that liquid water is more dense than ice.

Ice thus floats on water; this property has a simply incredible number of important consequences, not the least of which is that aquatic life can survive the winter in ponds in cold climates.

While liquids and solids have, roughly speaking, the same densities, the densities of gases are very much smaller. The mass of a cubic meter of a gas such as air under ordinary atmospheric pressure is about one kilogram, roughly 1000 times smaller than the density of water. The density of hydrogen is roughly 12,000 times smaller than that of water, while helium is 6000 times lighter than water. Because of these low densities, if a gas is released in a liquid, bubbles of gas rise to the top.

CRYSTALS

g. The crystal as a reflection of the building block

Few things in nature can compare in beauty with the interior of a geode, with its mass of amethyst crystals. As we look at these crystals, it seems that they all look alike and, then again, they don't look alike. Some of the crystals are short and squat, others are elongated. Yet with all this variety, as we carefully study the crystals, we come to realize that it is the angles between the faces of the crystals that are the same. Nicholas Steno discovered this law two hundred years ago (1669). The law is a consequence of the fact that a crystal is built up of tiny building blocks called unit cells. The unit cell is a parallelopiped, much like a brick, but the angles between the faces of the unit cell do not have to be right angles. Within this unit cell, the particles that compose the substance are arranged in the special way that is appropriate for this particular substance. The crystal is built up by repeating the unit cell in three dimensions. It is this repetition and the shape of the unit cell itself that leads to the constancy of interfacial angles.

In the interview, Dan Appleman, the Smithsonian geologist, uses the expression "the chemical elements" in describing the structure of crystals, liquids and gases. At this stage of our study, it will be clearer to interpret that phrase as "the particles".

HANDS ON

1. *Place a few ice cubes in a glass of water. Note that the water cools. Explain why.*

2. *Next time you step out of the shower, note how cold you feel. Explain why.*

3. *Place a few drops of water on the back of your hand. Spread them out with your finger tips. Then blow on the water. For comparison, blow on the back of your other hand. Note the difference in the two effects. Repeat the experiment using rubbing alcohol or vodka instead of water. These last two liquids are more volatile than water, so the cooling effect is enhanced.*

4. *The gas grills that are so popular for outdoor cooking are often fueled by a small tank containing liquid propane. The liquid propane is stored at ambient temperature but under high pressure. Opening the valve of the tank to supply the burners lowers the pressure and some of the liquid propane evaporates. Pick up the tank and shake it. What is inside the tank? Before opening the valve, feel the outside of the tank. Note the temperature. Open the valve and light the burners. After the gas has been burning for a while, feel the outside of the tank again. Do you notice any change in the temperature? How do you account for this?*

5. *Check the tire pressure on your car before and after driving at the speed limit for a while. Feel the tire before and after. Explain your observations.*

6. *Take a drinking glass with a smooth rim and fill it until the level projects a bit above the edge of the glass. Slide a card over the edge of the glass so that it covers the glass. While holding the card against the top of the glass, turn the glass upside down and take your hand away from the card. (Note: Best to do this over a sink until you master the trick.) Why does the water stay in the glass?*

QUESTIONS

1. *At ordinary temperatures and pressures the volume occupied by a gas is about 1000 times the volume occupied by the same mass of the same substance as a liquid or solid. What does this tell you about the occupation of the space in the three states of matter? What does it tell you about the relative density of a gas compared to a solid or a liquid?*

2. *What effect does increasing the temperature of a gas have on the molecular motion?*

3. *What does the boiling point tell us about the forces acting between the particles of a substance?*

UNIT 6

THE ATOM

BEFORE WATCHING

YOU ALREADY KNOW

Atoms are the ultimate building blocks for all substances.

Mass is conserved in chemical reactions.

READ

Chapter 3: Atoms (entire chapter)

OVERVIEW

The earliest model for the structure of matter was an "atomic" model suggested by Democritus, a fourth century B. C. Greek philosopher. The proposition was based on a **philosophical** argument. If one takes a piece of matter and cuts it in half, the two pieces produced differ from the original piece only in their size but not in any of their other properties. Repeat the procedure and the same is true. The piece of matter could be cut into smaller and smaller pieces and still retain its identity. But it seemed to Democritus that the process could not be repeated indefinitely; at some point the pieces would be so small that they could not be cut into smaller pieces without the substance losing its identity. He called these ultimate particles **atoms,** from the Greek prefix, **a**- signifying privation, and the Greek word **tomos,** meaning **"cut"**. The word, **atom,** means literally "not cut", or that which cannot be cut.

In this program, we present some of the experimental evidence for our modern model of the atom. We describe the way the elementary particles (electrons, protons, and neutrons) are arranged in the atom. The electrons are given special attention because it is the occupation of energy levels by electrons that determines the chemical properties of an atom. This modern "wave-mechanical" model of the atom was proposed by Schroedinger and Heisenberg in 1927. It should be understood that the modern model is not a planetary model. We know the energies

of the electrons in the atom, but we do not know any of the details of the motions of the electrons around the nucleus. The best we can do is to say what the chances are of finding the electron in a specified element of volume. In this sense, our modern model is a statistical model. Finally, we present applications of this knowledge to spectroscopy and to the imaging of atoms by scanning tunnelling microscopy.

WHAT TO LOOK FOR:

DALTON'S ATOMIC THEORY

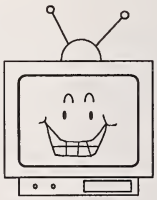
a. conservation of mass
b. law of definite proportions

STRUCTURE OF THE ATOM

c. electrons, protons and neutrons
d. the scanning tunnelling microscope
e. electrical charge
f. the Rutherford experiment

ELECTRON CLOUDS

g. the motions of the electrons
h. energy
i. a model for understanding spectra



WATCH THE PROGRAM

AFTER WATCHING

DALTON'S ATOMIC THEORY

a. conservation of mass

Dalton's atomic theory was designed to interpret the quantitative data about chemical reactions that were available at that time. Dalton assumed that the atoms of each element persisted through chemical change and carried their characteristic weights with them. That is, there were the same number of atoms of each element before and after a chemical change. It was only that the atoms were somehow connected differently. Thus, since the atoms are conserved in the reaction and each atom has its characteristic weight, weight (mass) is conserved in the reaction. (Again, remember that we are using mass and weight synonymously.)

b. law of definite proportions

The law of definite proportions simply says that the elements combine to form compounds in definite ratios by weight. For example, when hydrogen and oxygen combine to form water the weight ratio is always 8 grams of oxygen to 1 gram of hydrogen; we have even observed this same ratio in the water found in interstellar space. This weight ratio is always the same. Dalton's statement that atoms of one element combine with atoms of another element to form compounds in ratios of small whole numbers together with the statement that the atoms of an element have characteristic weights is sufficient to predict the law of definite proportions.

STRUCTURE OF THE ATOM

c. electrons, protons and neutrons

Our current model views the atom as a composition of three fundamental particles: the electron, the proton, and the neutron. The diameter of an atom is of the order of 100 picometres (pm) (1 pm = 10^{-10} m). Centered in this atom is a tiny nucleus, about 0.01 pm in diameter. Surrounding the nucleus is an electron cloud. This electron cloud is what gives the atom its large size relative to the nucleus. The massive particles, protons and neutrons, exist only in the nucleus. The light particle, the electron, exists only outside the nucleus.

In the simplest atom, the hydrogen atom, there is one proton in the nucleus and one electron in the space around it. Note that the atom must not have a net electrical

charge; consequently, there must be as many electrons in the cloud as there are protons in the nucleus. Suppose we adopt the mass of the proton as our mass unit. Then the mass of the hydrogen atom is one mass unit. The next simplest atom is helium; there are two protons and two neutrons in the nucleus, giving the atom a mass of four mass units (note that neutrons have very nearly the same mass as protons). To balance the positive charge on the nucleus, there must be two electrons in the electron cloud.

The next heaviest atom is the lithium atom; it has 3 protons and 4 neutrons in the nucleus, giving it a mass of 7 units. It must have 3 electrons in the electron cloud to balance the charge of the nucleus.

We know now that the property that distinguishes between the elements is the number of protons in the nucleus (this number is called the "atomic number"). Dalton's theory proposed that it was the mass that characterized the elements. Today we know that atoms of the same element can differ in mass. Atoms of the same element which differ in mass are called **isotopes**. For example, there are three isotopes of hydrogen; each nucleus has one proton, but the number of neutrons is zero, one, and two. The masses are one, two, and three units respectively. The names are hydrogen, deuterium, and tritium. Since the chemical properties of any atom are determined by the numbers of electrons in the electron cloud, isotopes have the same chemical properties.

d. the scanning tunnelling microscope

The extraordinary images produced by the scanning tunneling electron microscope (STM) are images of the electron clouds around the atoms on the surface of the sample. Earlier we saw atoms only in our mind's eye; we believed that they would appear in such a way if we could see them. Based on our belief of how the atom should look it was possible to design the instrument that produces these images. The simplicity of the instrument is a tribute both to our knowledge and to our technology.

e. electrical charge

The phenomenon of static electricity was apparently first described by Thales of Miletus, a Greek philosopher of the sixth century B. C. When amber was rubbed with a cloth, it attracted light objects such as dust. This phenomenon of electrification takes its name from **elektron,** the Greek word for amber. Later, it was discovered that if glass was rubbed with silk it also became electrified, but the behavior was different. The ancients distinguished between "resinous" and "vitreous" electricity. Benjamin Franklin gave us the modern names, negative and positive, that distinguish between the two kinds of electrical charge. As the demonstration in the film shows, two bodies having the same kind of charge will repel each other while two bodies with different kinds of charges will attract. Like charges repel; unlike charges attract.

The invention of the "voltaic pile" in the late 1700s was soon followed by the discovery that passing an electrical current through a chemical system could produce a chemical reaction. This was followed by a large amount of work on electrolysis, chemical reactions produced by passage of an electrical current. By the 1830s it was clear that chemical changes were intimately connected with electrical charges. For example, using Faraday's laws of electrolysis, we could calculate how much electrical charge had to be passed through a chemical system to effect a specified amount of chemical change.

The discovery of the electron by J. J. Thomson in 1897 gave us the first chance to begin the exploration of the interior structure of the atom. The apparatus is depicted in the program. If an electric current is passed between two electrodes in a glass tube from which all the gas has been removed, the glass glows. Insertion of obstructions in the tube and observation of the shadows that they cast soon makes it clear that a beam of particles is being emitted from the negative electrode. By imposing electric and magnetic fields across the beam we can demonstrate that the particles in the beam are negatively charged and we can measure the ratio of the electrical charge to the mass of the particle.

A similar apparatus containing hydrogen gas under a very low pressure can be arranged in such a way as to produce a beam of particles, called protons, that have a positive electrical charge. Ultimately, it was possible to show that the electrical charges on the electron and proton were equal in magnitude but opposite in sign and that the mass of the proton is 1837 times greater than the mass of the electron.

Many years later, a third particle, the neutron, was discovered. The neutron has no electrical charge; its mass is essentially the same as that of the proton.

f. the Rutherford experiment

In the Rutherford experiment a beam of positively charged particles (alpha particles) is sent through a very thin gold foil. The result was astonishing. At the time this experiment was done, there was no accepted model of the atom. The ones that had been proposed all were subject to objections on fundamental grounds. The atom was thought of vaguely as a kind of mush of positive and negative particles, immersed in some neutral material. Now, if one shoots a positively-charged bullet (the alpha particle) through this material (the gold foil) then one would expect the result would be much like shooting an ordinary bullet through a bale of cotton. Most of the bullets would simply go straight through and come out the other side. A few would be deviated slightly from that path. No one expected the real result, that a few of the bullets would be bounced back in nearly the same direction as that from which they came.

Once this observation had been made, Rutherford was able to show by a direct classical calculation that all the positive charge and all the mass of the atom must be concentrated in an extremely small fraction of the space occupied by the atom; this massive, positively charged region is called the nucleus.

THE ELECTRON CLOUD

g. the motions of the electrons.

Following the proposal of the nuclear model of the atom by Rutherford, Bohr proposed a planetary model for the electron motions. He simply ignored the classical objections to such a model. There was an important difference between Bohr's model and the classical planetary system. In a planetary system the radius of the orbit can have any value. In Bohr's model only certain orbits were allowed. This in turn meant that the energy of the electron could only have special values and not others.

Later, in 1927, Schroedinger and Heisenberg proposed the "wave-mechanical" model of the atom. The modern form of this model that is still in use today. It shares with the Bohr model the idea that only certain states are allowed. However, it does not describe these states in terms of orbits. It is a central feature of the theory that we cannot know the details of the motion of the electrons.

h. energy

Consider the hydrogen atom in its lowest possible energy state (this is called the "ground state" of the atom). The electron cloud in this case is spherical, centered on the nucleus, and looks a little like a ball of cotton. But the cloud does not have a uniform density throughout. The question we can ask is, "What is the chance of finding the electron at a given distance from the nucleus?" The answer is that there is no chance of finding the electron at the nucleus; as we walk away from the nucleus the chance of finding the electron gets larger, goes through a maximum value and then decreases rapidly so that the chance of finding the electron far away from the nucleus is again zero. This probabilistic description of the electron's position is a direct consequence of the wave-mechanical model and is not derivable from any model involving classical planetary motion.

The spherical cloud is called an "s cloud". (The "s" is derived from the initial letter of the word, sharp, used by the spectroscopists of the 19th century to describe a particular series of lines in atomic spectra.) In any atom there is a series of these s-states which the electron can occupy; each of them has its own characteristic energy and all of them yield a spherical electron cloud. It is customary to think of the energies of these states as being arranged on a vertical scale in increasing order of energy. This gives us a series of **energy levels** in which the electron can reside.

If an atom interacts with a light beam having the right frequency to raise the energy of the electron to another permitted state the shape of the cloud changes. Instead of being spherical, this new cloud has axial symmetry. It looks like a "figure 8" that has been rotated around the vertical axis to generate a figure that looks like a dumbbell. Again, the cloud does not have the same density throughout. This new state in which the electron finds itself is called a p-state. Again, there is a series of these p-states whose energies we can arrange in increasing order, giving another

series of energy levels in which the electron can reside. In all of these p-states the electron cloud is dumbbell-shaped. It should be mentioned that these p-states occur only in sets of three.

There are other energy states in which the electron clouds have more complicated shapes, but all are symmetric about the vertical axis.

i. a model for understanding spectra

In the animation in the program, only one s-state and one p-state are shown. The transition between the two states is effected by the absorption or emission of light. The light beam carries its energy in small packages, called **quanta**. (Singular form is "quantum".) The energy of the quantum of light is inversely proportional to its wavelength; the shorter the wavelength, the higher the energy. By choosing the proper wavelength (i.e. the proper color), we can select light whose quanta can supply exactly the correct energy to lift the electron from the s-state to the p-state. This light will be absorbed by the atoms. Conversely, an atom in the p-state can jump down to the s-state and emit a quantum of light of a wavelength (color) corresponding to the difference in energy between the p-state and the s-state.

Thus, we have a very simple model of the atom which we can use to understand the spectra exhibited by atoms. The model has the following features:

1. Associated with every atom are several series of energy levels. According to the rules of wave mechanics, each of these energy levels can be occupied by no more than two electrons.
2. In its lowest energy state (its "ground state"), the electrons in the atom fill the lowest energy levels until all the electrons are assigned to some level. The higher energy levels are vacant.
3. A beam of light carries energy in small packages called "quanta". The energy of the quantum is inversely proportional to the wavelength of the light. This means that a quantum of red light has a relatively low energy, while a quantum of violet light has a relatively high energy.

The model can be used in the following ways.

Suppose that we send a stream of light quanta into a collection of atoms. If a quantum of light hits an atom and has exactly the right energy to lift an electron from one energy level to a higher one, then that light quantum will be absorbed by the atom and its energy will be converted into energy of the atom (the electron is moved to a higher energy level).

In atoms with many electrons, there are many different ways to lift electrons from one level to another and so there are many possible wavelengths that can be absorbed. The absorption spectrum appears to be quite complicated, but it can be interpreted in terms of an energy level diagram.

Similarly, if we put a sample of the element into the arc between two electrodes, many electrons are moved to higher energy levels. Once they are in these upper levels, these electrons can drop back to lower, vacant energy levels. In doing so, light quanta of various wavelengths will be emitted; this pattern of wavelengths is called the emission spectrum of the element. Again, the wavelength of the emitted light is determined by the difference in energy between the two energy levels.

Since the energy levels are different in the atoms of different elements, the absorption and emission spectra are characteristic of the element and can be used to identify it.

HANDS ON

1. *Observe the "neon" lights in various advertising signs. Note that only the red ones contain neon. The lights of other colors contain other gases.*

2. *Observe the high intensity green and yellow lights used in illuminating highways and streets. The green ones contain mercury vapor and the yellow ones contain sodium vapor.*

QUESTIONS

1. *Will a proton and an electron attract or repel each other? Why?*

2. *What did the Rutherford experiment demonstrate?*

3. *In which part of the atom are the electrons?*

4. *What happens to the electron if a quantum of light is absorbed by the atom?*

5. *What happens to the electron when a quantum of light is emitted by the atom?*

6. *Which quantum of light will have the higher energy, a short wavelength quantum or a long wavelength quantum?*

UNIT 7

THE PERIODIC TABLE

BEFORE WATCHING

YOU ALREADY KNOW

Atomic number

Atomic mass

Electron clouds

READ:

Chapter 4: Elements in Useful Order—The Periodic Table (entire chapter)

OVERVIEW

The periodic table is a chart used by chemists to organize our knowledge of the chemical properties of the elements. The program presents some of the main features of the table.

At first glance, the amount of information printed in the periodic table for any one element would seem to be negligible. In many versions of the table, the symbol for the element, its atomic number and its atomic mass* are the only items printed. It would seem that this information could be more efficiently conveyed in a listing of the elements alphabetically by name. The key to the usefulness of the periodic table lies in the **pattern** in which the elements are arranged. This pattern in itself is a way to store information about the chemical properties of the elements.

An industrial application of the periodic table is presented; some trends in properties are shown.

Finally, the basis of the periodic table, the electron arrangements in the atoms, is illustrated, and an analytical application based on this knowledge of electron arrangements is described.

* We will use atomic mass and atomic weight synonymously.

WHAT TO LOOK FOR:

THE PERIODIC TABLE

a. why do we need a periodic table?
b. what information does it contain?
c. nomenclature and arrangement of the table

USES OF THE PERIODIC TABLE

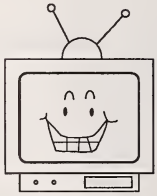
d. similarities and trends in groups and periods
e. application to glassmaking

HISTORICAL

f. Mendeleev
g. Seaborg

ENERGY LEVELS

h. levels
i. rules for filling the levels
j. chemical properties defined by the outer electronic arrangement
k. application: X-ray fluorescence spectroscopy



WATCH THE PROGRAM

AFTER WATCHING

THE PERIODIC TABLE

a. Why do we need a periodic table?

In the nineteenth century there was an enormous amount of chemical experimentation. The knowledge gained from all these experiments needed to be organized. By the middle of the nineteenth century chemists began to see relations between the properties of the elements. In the 1860s the first attempts were made to arrange the elements in patterns that grouped elements with similar properties together in families.

b. What information does the periodic table contain?

Although there are some elaborate versions of the periodic table in which values of physical properties such as density, melting points, boiling points, electronic structure, as well as other data, are printed, the most common versions print only the atomic number, the symbol for the element, and the atomic mass. How then can we say that the periodic table summarizes our knowledge of chemical and physical properties of the elements? The location of each element in the table gives information on its properties. Thus, the pattern itself is the way the periodic table stores chemical information.

c. Nomenclature and arrangement of the table.

The elements are arranged in the table in order of increasing value of their atomic number, that is, by the number of protons in the nucleus. Suppose that we write down the symbols for the first few elements horizontally:

H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar

Ignore hydrogen, symbol, H, for the moment. As the first element hydrogen is unique and doesn't fit unambiguously in the pattern as do the other elements. As chemists, we look at this list and realize that helium, He, is similar chemically to neon, Ne. Also, lithium, Li, is similar to sodium, Na. The similarities persist through the series. So we write these elements in two rows, one underneath the other:

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	C
Ar							

In this array, elements that are chemically similar fall in the same column. These columns are called "groups" or "families". Earlier, the left-hand column containing helium, neon, and argon, was called "Group 0"; today we know that it is more logical to move it to the right-hand side and call it "Group VIII". The rows are called "periods". When we do this the array becomes:

	I	II	III	IV	V	VI	VII	VIII
1	H							He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar

Roman numerals are used across the top to label the groups, and Arabic numerals are used at the left to label the periods.

If we attempt to continue this construction, we find that the next two elements, potassium and calcium (K and Ca), fall nicely in Groups I and II, where they belong, but the next ten elements do not follow the pattern. The pattern only resumes after the insertion of ten elements. This happens not only in Period 4 but also in Period 5. The result is:

	I	II		III	IV	V	VI	VII	VIII
1	H								He
2	Li	Be		B	C	N	O	F	Ne
3	Na	Mg		Al	Si	P	S	Cl	Ar
4	K	Ca	...ten elements...	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	...ten elements...	In	Sn	Sb	Te	I	Xe

It should be understood that the ten columns formed by the inserted elements contain ten new chemical families.

Life becomes more complicated in Period 6, in which 24 elements (10 and then 14 more) are interpolated before the pattern on the right is resumed. We need not be concerned with all these details. The reasons will become apparent when we look at the modern model of the atom.

d. Similarities and trends in groups and periods.

We have remarked before that the chemical properties of the elements in any group (column) are very similar to one another. The elements in Group I (again, ignore hydrogen) were shown in Don Showalter's demonstration. All these elements are very reactive towards air, water, and many other substances. Since they are so reactive, they are stored under kerosene, an inert hydrocarbon liquid, that shields the metals from contact with air and moisture. The metals become more reactive as we go down the column. Rubidium and cesium burst into flame on contact with air

and so are stored in sealed glass ampoules under an inert gas atmosphere. Even potassium, if spread in a thin layer, will catch fire in air. The demonstration of the reaction of lithium, sodium, and potassium showed dramatically the increase in rate of reaction with water.

$$2M + 2H_2O \longrightarrow 2MOH + H_2$$

(The symbol, M, stands for any of the metals in question.)

On contact with water, lithium reacted fairly rapidly, sodium, much more rapidly and potassium exploded. So there are not only similarities in properties but there are regular trends in these properties as we move through the group.

The elements in Group I all behave as metals. Their melting and boiling points decrease as we go down in the group; lithium melts at 186 °C, while cesium melts only slightly above room temperature at 28.5 °C. The sizes of the atoms increase as we go down in the group.

In contrast to the elements in Group I, which are all solid metals, the elements in Group VII are nonmetals; fluorine and chlorine are gases, bromine is a liquid, and iodine is a low melting solid. None of these elements react with air under ordinary circumstances. Again, just as in the case of Group I, the size of the atoms increases as we go down in the group.

In Group VII, the topmost element, fluorine, is the most reactive, reacting with almost everything but air. Chlorine and bromine are somewhat less reactive; they corrode most metals rapidly and react readily with water. Iodine undergoes these reactions much more slowly.

e. Application to glassmaking

Ordinary soft glass is produced by combining sand (silicon dioxide), soda ash (which at glass making temperatures decomposes into sodium oxide), and lime (calcium oxide). When these oxides are melted together, the result is a transparent substance which is soft at high temperatures and can be blown into bottles or other shapes, or can be rolled into sheets for use as window panes.

The properties of the glass depend on the relative proportions of the major constituents as well as the presence of minor constituents; for example, the addition of lead oxide results in a more brilliant glass used in cut glass articles. Pyrex glass is a glass in which a substantial portion of the silicon dioxide is replaced by boron oxide and a small amount of aluminum oxide. The result is a glass that expands relatively little with increase in temperature. It can therefore be heated and cooled without breaking; it is used for cookware.

Using the periodic table as a guide, the glass chemist in the program is able to suggest what kind of substitution could be made in the formulation of the glass to produce a desired result. Originally a highly empirical chemical art, glassmaking has moved into the realm of science.

HISTORICAL

f. Mendeleev

Following Lavoisier's establishment of the law of conservation of mass and Dalton's proposal of the atomic theory at the opening of the nineteenth century, an enormous amount of chemical experimentation resulted in a large accumulation of knowledge about chemical properties. By the 1860s many attempts were being made to systematize this knowledge. Since there was no theoretical basis to guide these attempts, most of them were unsuccessful. Two men, Dimitrii Mendeleev and Lothar Meyer, came up with substantially the same version of what is now called the periodic table. We shall devote our attention to Mendeleev's efforts.

In his attempt to organize all this diverse knowledge, Dmitrii Mendeleev wrote down the important properties of each known element on a separate card. He played with these cards, arranging and rearranging them over and over again. Ultimately, Mendeleev discovered a quite remarkable thing. He arranged the cards in increasing order of the atomic mass of the element. After the first eight cards were put down, the next element, the ninth, had chemical properties very similar to those of the second element, so he placed card number 9 under card number 2; similarly, the element on card number 10 was very similar to the element on card number 3, so card number 10 was placed under card number 3. This repetition of properties continued albeit in a more complicated way. In 1871 Mendeleev published what is essentially a modern form of the periodic table, or at least as modern as one could expect for 1871. A striking feature of this table were certain positions that Mendeleev left vacant, claiming that they belonged to elements as yet undiscovered. He even went so far as to predict the properties of these elements, one of which he called eka silicon. A comparison of the values he predicted for eka silicon with those of germanium, discovered in 1886, are given below:

Property	Eka silicon	Germanium
Atomic weight g/mol	72	72.6
Density g/cm^3	5.5	5.36
Formula of oxide	EsO_2	GeO_2
Density of oxide g/cm^3	4.7	4.228
Boiling point of $EsCl_4$	under 100 °C	84 °C

The remarkable accuracy of these predictions, as well as others, is a tribute not only to the correctness of the periodic law but to Mendeleev's chemical intuition.

g. Seaborg

The periodic table is a model; it is a way to represent reality. When we learn new things about reality, the model often needs to be changed. This happened with Glenn Seaborg in the 1940s.

In the early 1940s, using the methods of high energy physics, a number of new elements were synthesized by Glenn Seaborg and his associates. As more and more artificial elements were produced, and their chemical properties were studied, the question naturally arose as to which families in the periodic table they belonged. This question was answered in an unexpected way by Seaborg. He suggested that they belonged to a new series of elements, now called actinides. To understand this we must back up a little bit. (To follow the discussion below, it will be helpful to have the textbook open to display the periodic table.)

After element 57, lanthanum, there are 14 elements, called rare earths, elements 58 through 72, whose chemical properties suggest that they all belong in Group III with lanthanum. They are usually placed below the main body of the table. These 14 elements are called lanthanides. Now, if we look in the next period, the element below lanthanum is 89, actinium. Before Seaborg's suggestion, the next three elements, all of which occur naturally, were placed in Groups IV, V, and VI. Seaborg's suggestion, which has proved to be correct, was that these three natural elements, along with the newly synthesized artificial elements, belonged in a new series of 14 elements, analogous to the lanthanides. These elements are called actinides since they follow actinium in the periodic table. As Glenn Seaborg mentions in his relation of the episode, the suggestion encountered some opposition before it was finally accepted.

As of the beginning of 1989 the series of 14 actinides is complete and 6 other elements beyond that series have been made artificially, for a total of 109 elements.

We understand the patterns in the periodic table in terms of the structure of the atoms and, particularly, in terms of the **energy levels** in the atoms.

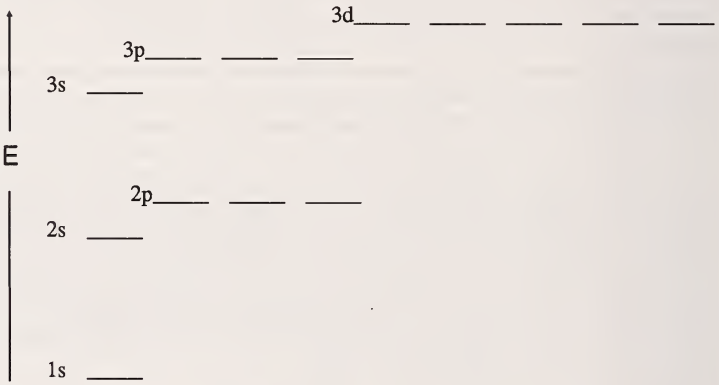
ENERGY LEVELS

h. Levels

The atomic number of an atom is the number of protons in the nucleus of the atom; this, in turn, is equal to the number of units of positive charge on the nucleus. This positive charge must be balanced by an equal and opposite negative charge so that the atom itself will be electrically neutral. This negative charge is provided by electrons, equal in number to the number of protons in the nucleus and each carrying a unit of negative charge. These electrons form a negatively charged cloud around the nucleus of the atom.

NOTE: Each electron forms an electron cloud and, as we saw in Program 6, the shape of this cloud is determined by the energy level of the electron. The actual cloud around the atom is a composite of the clouds produced by each electron.

In this cloud, the electrons may have certain definite values for their total energy; other values of energy are **not allowed**; we say that the electrons occupy **energy levels** in the atom. Below we show schematically the first few energy levels for an atom.



In this diagram, the energy increases in the vertical direction. Thus, the level labelled 1s has the lowest energy, while the levels labelled 3d have the highest energy of the levels shown. There are higher energy levels not shown in this diagram. There is no significance to the horizontal positions of the levels. They have been spread out horizontally simply to produce a less crowded diagram.

Note that the levels occur in sets; the sets are labelled with numbers. The lowest energy "set" contains only one level, the 1s level. The next higher energy set contains four levels, the 2s level and the three 2p levels. The 2s level is slightly lower in energy than the 2p levels. The next higher energy set contains nine levels; the 3s level, the three 3p levels, and five 3d levels. Of course, there are additional sets with numbers 4, 5, 6, and so on. Each set contains a larger number of levels than its predecessor. It is extremely important to realize that the electron can have an energy corresponding to any one of the energy levels in the atom, but **it cannot have any energy value that lies between the levels.** Finally, it should be mentioned that the vertical positions of the levels shift as we move from one element to the one of next higher atomic number, but the pattern of the levels remains

essentially the same. (The use of the letters, s, p, d, f, evolved from the spectroscopic notation developed a century ago.)

I. Rules for filling the levels

A fundamental law of nature is: **No more than two electrons can occupy any level.**

This pattern of energy levels enables us to understand why the periodic table is the way it is. Consider how we can arrange the electrons in the various levels, in every case requiring that the resulting atom have the lowest possible energy; that is, its electrons are placed in the lowest possible energy levels.

Hydrogen has one electron; it is placed in the lowest energy level, the 1s level. The next element is helium, with two electrons. Both of these electrons can go in the 1s level; but now the 1s level is filled because no more than two electrons are permitted in any level. The next element, lithium, has three electrons. To place these electrons in the lowest levels, we put two of them in the 1s level and the third in the next lowest level, the 2s level. We continue this procedure each time adding one more electron in the lowest available unfilled level. Thus, we can write a table of the electronic structures of the atoms; it looks like this: (The numbers under the symbol for the level are the number of electrons in the level.)

Element	Symbol	Atomic Number	1s	2s	2p	3s	3p
Hydrogen	H	1	1				
Helium	He	2	2				
Lithium	Li	3	2	1			
Berylium	Be	4	2	2			
Boron	B	5	2	2	1		
Carbon	C	6	2	2	2		
Nitrogen	N	7	2	2	3		
Oxygen	O	8	2	2	4		
Fluorine	F	9	2	2	5		
Neon	Ne	10	2	2	6		

Note that since there are three 2p levels they can accommodate a total of six electrons; two in each of the three levels.

In the program the "electron team" is used to give an animated illustration of the rules for filling the energy levels.

j. Chemical properties defined by the outer electronic arrangement

The chemistry of an element is determined by the electrons in the highest occupied energy levels. Thus, the chemistry of hydrogen and helium is determined by the electrons in the 1s level. The chemistry of the elements from lithium to neon is determined by the electrons in the 2s and 2p levels. Once the levels 2s and 2p are filled, as in neon, the resulting octet of electrons is chemically inert; neon has no chemistry. It does not form any compounds.

It is now easy to see how the repetition of chemical properties recorded in the periodic table is a consequence of the electronic structure of the atom. The element immediately following neon is sodium, with eleven electrons; ten of these electrons fill the 1s, 2s, and 2p levels, as do the ten electrons in neon, the eleventh electron must go in the next higher level, the 3s level. Thus we have:

Element	Symbol	Atomic Number	1s	2s	2p	3s	3p
Sodium	Na	11	<neon shell>			1	
Magnesium	Mg	12	<neon shell>			2	
Aluminum	Al	13	<neon shell>			2	1
Silicon	Si	14	<neon shell>			2	2
Phosphorus	P	15	<neon shell>			2	3
Sulfur	S	16	<neon shell>			2	4
Chlorine	Cl	17	<neon shell>			2	5
Argon	Ar	18	<neon shell>			2	6

In all of these atoms we have the filled electron shell of the neon atom overlaid by additional electrons in the 3s and 3p levels. It is the electrons in these higher energy levels that determine the chemical properties. The outer configuration of the sodium atom has one electron in the 3s level. This makes sodium similar in chemical properties to lithium, whose outermost electron is in the 2s level. In the same way, the outermost electrons in carbon are two in the 2s level and two in the 2p level; carbon is therefore similar in chemical properties to silicon that has two electrons in the 3s level and two electrons in the 3p level.

The outer filled shell of eight in argon is again chemically inert; argon like neon forms no chemical compounds.

Elements in the **same** group of the periodic table have the **same** arrangements of the outer electrons and have similar chemical properties.

Since there are five 3d levels, each can contain two electrons for a total of ten. So at this point we could expect a series of ten elements to be inserted before the next set of levels begins to fill. In fact, that does not happen. The 4s level fills first with the elements potassium and calcium and then, as we indicated above, a series of ten

elements (from scandium to zinc) is inserted. Then the filling of the 4p levels occurs, and we have the repetition of properties appropriate to partially filled p levels.

The fourth set of levels are the 4s, 4p, 4d, and 4f. The 4d, like the 3d, consists of five levels and can take ten electrons. The 4f consists of seven levels that can accommodate fourteen electrons. It is the filling of the 4f levels that accounts for the fourteen rare earth elements, the lanthanides.

k. Application: X-ray fluorescence spectroscopy

We can interpret the phenomena occurring in x-ray fluorescence spectroscopy in terms of this model of the atom, electrons in energy levels.

If a beam of x-rays impinges upon an atom, it can eject an electron from one of the lowest energy levels; for example, it can eject a 1s electron. This leaves a vacancy in the 1s level. An electron can fall from a higher level, such as the 2p level, to fill the 1s vacancy. When this happens, an x-ray is emitted. There is now a vacancy in the 2p level; an electron from a higher s or d level can fall down to fill this vacancy, again emitting an x-ray. This continues until there are no more electrons above the vacancy. The frequencies of the x-rays emitted depend on the energy difference through which the electrons fall. Since these energy differences are characteristic of the element, we can identify the element by this method. The frequencies emitted constitute the **x-ray fluorescence spectrum** of the element. The method has the advantage of being rapid and non-destructive, ideally suited for the analysis of the pigments in a painting, as described in the program. This method was also used to analyse portions of the moon's surface without bringing samples back.

HANDS ON

1. *Take a deck of playing cards. See how many different logical ways you can find to arrange the cards.*

2. *Take a child's set of colored blocks. How many different ways can you find to organize the blocks?*

QUESTIONS

1. *Most versions of the periodic table only contain the symbol of the element, its atomic number and its atomic weight. How does it convey information about chemical properties?*

2. *Looking at the periodic table, how many elements are in the first period? In the second period? Reconcile these numbers with the energy level diagram.*

3. *Looking at the table, give the chemical symbols for two elements that will have chemistries similar to that of calcium (Ca).*
   Give the symbols for two elements that will have chemistries similar to chromium (Cr).

4. *Looking at the table, which atom will be larger, the fluorine atom (F) or the chlorine atom (Cl)?*

5. *Follow in the footsteps of the electron team and write the electron configurations for beryllium (Be) and magnesium (Mg).*

6. *Describe what happens within an atom that produces the x-ray fluorescence spectrum.*

7. *"X-ray fluorescence is used to take the fingerprints of art work." Explain.*

UNIT 8

CHEMICAL BONDS

BEFORE WATCHING

YOU ALREADY KNOW

Electrons in the atom are arranged in energy levels.

The noble gases are chemically quite unreactive.

Chemical properties are determined by the electron configuration in the outer shell of the atom.

READ:

Chapter 5. "Ionic Bonds"; "Covalent Bonds"

OVERVIEW

The program addresses the question of how chemical bonds are formed. In general, this bonding occurs in two distinct ways: (1) by electron transfer from one atom to another, in which case we have an ionic bond, and (2) by sharing a pair of electrons between two atoms, in which case we have a covalent bond. It is important to note that the program deals only with these two extreme types of bonding.

Some properties of ionic compounds are demonstrated; for example, the difficulty of melting them and their electrical conductivity in the molten state and in aqueous solution.

The energy involved in forming stable bonds is demonstrated in the ionic case by the reaction of sodium with chlorine. In the covalent case the properties of explosives illustrate the difference in energy between different covalent bonds. Explosive compounds are unstable (high energy) nitrogen compounds which decompose violently to form stable (low energy) nitrogen molecules, water molecules, and carbon dioxide molecules. (All these compounds are formed as gases in the explosion.) The covalent bonds in the explosive compound are weaker than the bonds in the product molecules. The explosive compound has a high

energy content; the difference in energy between the high energy explosive and the low energy products is released in the explosion and conveyed to the gaseous products.

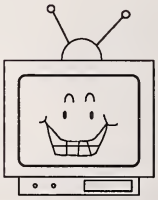
WHAT TO LOOK FOR:

IONIC COMPOUNDS

a. from atoms to ions
b. sodium and chlorine react
c. electrical conductivity
d. crystals of salt and of calcite

COVALENT BONDS

e. from atoms to molecules
f. nitrogen compounds as explosives
g. nitrogen fixation



WATCH THE PROGRAM

AFTER WATCHING

IONIC COMPOUNDS

a. from atoms to ions

In Program 7 we called attention to the chemical inertness of the filled shells of eight electrons (two s electrons and six p electrons). It turns out that we can interpret a good deal of chemistry, especially of the elements in the first three periods, in terms of the stability of the filled shell of eight. Consider the atom of sodium; it has the electron configuration:

	1s	2s	2p	3s
Na atom	2	2	6	1

When the 3s electron, which is the outermost electron in the atom, is removed the remaining entity is called a sodium **ion** and is symbolized by Na^+.

$$Na \longrightarrow Na^+ + e^-$$

This sodium ion has a filled shell of eight outermost electrons.

	1s	2s	2p	3s
Na^+ ion	2	2	6	

This filled shell of eight is very stable chemically, so the sodium ion does not lose any more of its electrons.

Metals in general tend to lose electrons with ease to form positive ions.

Now consider the atom of chlorine; it has the electron configuration:

	1s	2s	2p	3s	3p
Cl atom	2	2	6	2	5

If one electron is added to the chlorine atom, a chloride **ion** is formed, which has a negative charge and is symbolized by Cl^-.

$$Cl + e^- \longrightarrow Cl^-$$

This chloride ion has a filled shell of eight outermost electrons.

	1s	2s	2p	3s	3p
Cl^- ion	2	2	6	2	6

Just as in the sodium ion the filled shell of eight in the Cl^-ion is very stable chemically.

Nonmetals, the elements on the right-hand-side of the periodic table, in general accept electrons easily to fill their incomplete electron shell and form negative ions; examples are chlorine and oxygen.

How, then, is the compound, sodium chloride, formed from sodium and chlorine? An electron is **transferred** from a sodium atom to a chlorine atom, in the process forming a sodium ion and a chloride ion. These ions have opposite electrical charges and so attract each other. Each sodium ion attracts as many chloride ions around it as possible; similarly, each chloride ion attracts as many sodium ions around it as possible. Geometry limits the number of ions that can get close to the oppositely-charged ion and the final result is that a sodium chloride **crystal** builds with six chloride ions around each sodium ion and six sodium ions around each chloride ion. The pattern of ions in the crystal has the symmetry of a cube. A drawing of the structure is shown in the program.

A considerable amount of energy is released in this transformation, since the salt, NaCl, is much more stable than the elements.

The removal of an electron from a neutral atom such as sodium produces a positive ion that is markedly smaller than the neutral atom. This shrinkage occurs simply because it is the outermost part of the electron cloud that is removed. The remainder of the electron cloud, the inside part, is smaller.

The addition of an extra electron to a neutral chlorine atom increases the total repulsion between the electrons and this causes the electron cloud to swell.

b. Sodium and chlorine react

In this dramatic demonstration, metallic sodium is melted and then is immersed in a flask of greenish-yellow chlorine gas. The metal burns in the chlorine atmosphere with a brilliant yellow flame, forming a cloud of white, solid sodium chloride, NaCl. A good deal of energy is released in the form of heat and light in the formation of this compound.

c. electrical conductivity

The demonstration in which the sodium chloride and the sugar are melted in the two crucibles fitted with electrodes shows that the molten sodium chloride conducts a current (the light lights) and the molten decomposing sugar does not conduct a

current. This tells us that in molten sodium chloride electrically charged particles are free to move, while in the molten sugar there are no mobile charged particles. Similarly, in an aqueous solution of sodium chloride the ions are free to move and the solution conducts a current.

d. crystals of salt and calcite

It is characteristic of ionic compounds that with a little care very large, almost perfect crystals can be grown. Sodium chloride is a cubic crystal; the symmetry of the macroscopic crystal is a consequence of the symmetry in the arrangement of the individual ions. Similarly, the rhombic crystal of calcite is a consequence of the way the calcium ions, Ca^{2+}, pack together with the polyatomic carbonate ions, CO_3^{2-}.

Even the small ionic crystals that we see in a salt shaker, for example, consist of enormous numbers of positive and negative ions.

COVALENT BONDS

e. from atoms to molecules

We can make two points about the formation of a covalent bond between two hydrogen atoms. First, note that the bond in the molecule consists of an electron cloud that is located between the two atoms that are bonded; the electron pair that makes up the cloud is **shared** between the two atoms. The second point is that when two separate atoms form a bond, the energy of the resulting molecule is always lower than that of the atoms. For this reason, the molecule is shown lower on the energy scale than the separated atoms.

Covalent bonds are formed between atoms that do not differ greatly in their tendency to gain or lose electrons. Thus, we may find covalent bonds between atoms of the same kind; for example, between two hydrogen atoms. Other examples of such diatomic molecules are N_2, O_2, Cl_2, and Br_2. Covalent bonds are not restricted to bonding the same kind of atom, but are found often between nonmetal atoms, especially between carbon, hydrogen, oxygen and nitrogen.

The covalent bond involves a pair of electrons that are shared between the atoms that are bonded.

f. nitrogen compounds as explosives

Elementary nitrogen consists of diatomic nitrogen molecules, N_2. The two nitrogen atoms are held together by a **triple bond**. A triple bond consists of three pairs of electrons that are shared between the two nitrogen atoms. The molecule is usually represented by

:N ::: N:

This triple bond is very stable. Since this bond is so strong, it is very difficult to break it. Thus, diatomic nitrogen, N_2, tends to be inert and does not easily react with other substances. The other side of this coin is that many nitrogen compounds, particularly organic nitrates such as cellulose nitrate, nitroglycerine, and trinitrotoluene (TNT), are unstable.

These materials are explosive because the bonds holding the nitrogen atoms to oxygen atoms are relatively easily broken; the nitrogen atoms are then free to combine with other nitrogen atoms to form the very stable nitrogen molecule, N_2. The oxygen atoms combine with any hydrogen to form water or with carbon to form carbon monoxide or carbon dioxide.

A large amount of energy is released when this happens; this energy release, together with the formation of gases such as nitrogen, water vapor, and carbon monoxide and carbon dioxide, makes these materials explosive. When these gases are formed at high temperature in the small volume originally occupied by the solid material, the pressure exerted by the gases is enormous; an expansion to a huge volume is required to bring the gases to atmospheric pressure. This is what produces the explosion.

Nitrogen triiodide, NI_3, is an unstable nitrogen compound. The compound exploded when the demonstrator touched it with a feather. (The purple iodine vapor formed is visible after the explosion.) The reaction is:

$$2NI_3 \longrightarrow N_2 + 3I_2 + \text{energy}$$

The bonds between the nitrogen atom and the iodine atoms are very weak compared to the bonds between nitrogen atoms in N_2 and between iodine atoms in I_2. Since both the nitrogen and the iodine are formed as gases, they must undergo a huge expansion to come to atmospheric pressure. This expansion produces the explosion.

Ammonium nitrate is another example of an inorganic substance that is useful as an explosive.

g. nitrogen fixation

Elemental nitrogen, N_2, is a very stable molecule and therefore is relatively inert chemically. Most plants and animals cannot use nitrogen as such. Still, plants and animals need nitrogen in usable forms to synthesize protein. There are a few plants, legumes for example, that are infected with bacteria that can take in nitrogen gas and convert it to ammonia. Ammonia is a nitrogen compound that a plant can use. There are also some bacteria that can convert nitrogen to nitrates and nitrites, which plants can also use.

Electrical storms, which produce nitrogen oxides and ultimately nitric and nitrous acids, serve as another source of usable nitrogen.

For modern high production agriculture, we cannot rely on the nitrogen compounds made naturally. We are dependent on synthetic fertilizers such as liquid ammonia and solid ammonium nitrate. To synthesize ammonia from elemental nitrogen requires high temperatures and therefore an energy input, as well as a catalyst, for the reaction to go. The nitric acid needed to make ammonium nitrate is obtained by the oxidation of ammonia. Therfore, we see that ammonia is an extremely important substance in our modern economy. We will deal with the ammonia synthesis in more detail in Program 14.

HANDS ON

1. *Pick out several solids (powders) from various places in your home. Can you decide whether they are ionic or covalent? Is the label of any help?*

2. *Some beautiful ionic crystals can be prepared by boiling a quarter of a cup of water, and stirring in sufficient Epsom salts (magnesium sulfate) until no more dissolves. Remove from the heat and stir in one or two drops of liquid glue. Using a wad of cotton, swab some of the liquid on a piece of glass. In a few minutes, crystals will start to grow in the liquid.*

QUESTIONS

1. *Why does chlorine exist as a diatomic molecule while argon exists as a single atom?*

2. *What is the raw material from which chlorine is produced? Name at least two other substances that are produced from this material.*

3. *Explain why the chemical reactivity of nitrogen depends on the strength of the triple bond but its boiling point does not.*

4. *Is the bond between oxygen and a metal such as potassium ionic or covalent? Why?*

5. *At very high temperatures the element selenium (atomic number 34) exists as a gas composed of Se_2 molecules. What kind of covalent bond holds the Se_2 molecule together?*

UNIT 9

MOLECULAR ARCHITECTURE

BEFORE WATCHING

YOU ALREADY KNOW

Covalent bonds are formed by the sharing of one, two, or three electron pairs between two atoms.

READ:

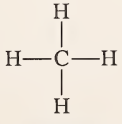
Chapter 5: "Predicting Shapes of Molecules"

Chapter 12: "Alkenes"; "Geometric Isomers in Alkenes"; "Optical Isomers"

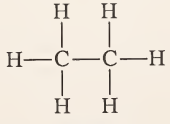
OVERVIEW

This program looks at some simple ideas about the shapes of molecules and examines some of the practical consequences of a molecule having a particular shape. One of these consequences is the existence of isomers. Isomers are molecules having the same numbers of atoms of the various kinds but which differ in the way the atoms are arranged in space. In this program we will deal with two kinds of isomerism; geometric, or **cis-trans**, isomerism and optical isomerism.

The simplest stable compound of carbon and hydrogen is methane, CH_4. The shape of this molecule is best described as a tetrahedron with the carbon atom at the center and the hydrogen atoms at the four apices. The compound ethane, C_2H_6, can be described in terms of two interlocking tetrahedra with hydrogen atoms at the remaining six corners. The two carbons are connected by a single bond.

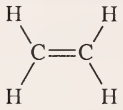


methane



ethane

If the two carbon atoms are connected by a double bond, as in ethylene, C_2H_4, then the configuration around the carbon atoms is triangular; the two overlapping triangles lie in the same plane, with the four hydrogen atoms at the remaining corners of the triangles.



ethylene

A compound such as ethylene with a double bond is said to be unsaturated; by adding hydrogen to the double bond we can produce the saturated compound, ethane. The presence of the double bond in a molecule can produce isomerism. In a long chain molecule, one isomer will have a bend or a kink in the chain while the other isomers will be straight. As a result, the properties of the two isomer will be different.

The demonstration shows that by adding hydrogen and removing the double bond we can convert a liquid vegetable oil with bent molecules to a solid fat with straight molecules.

In the second part of the program, the consequences of optical isomerism are developed. The effect of a sugar solution on a beam of polarized light is demonstrated. It is also shown that yeast cannot deal with the "wrong" optical isomer of glucose (L-glucose). The specificity of the enzyme in the yeast is thus demonstrated. The fact that organisms produce molecules consisting only of one type of optical isomer and not the other is discussed.

Finally, racemization, the transformation of a pure optical isomer into a mixture of the two possible isomers, is described in connection with its application to the dating of fossils.

WHAT TO LOOK FOR:

SHAPES OF MOLECULES

a. covalent bonding and geometry
b. methane and ethane
c. ethylene

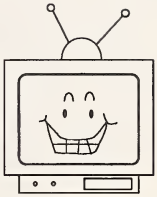
FATS AND OILS

d. saturated and unsaturated fats and oils
e. models of saturated and unsaturated fatty acids
f. hydrogenation of a vegetable oil
g. isomerization of unsaturated fatty acids

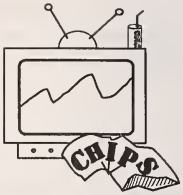
OPTICAL ISOMERS

h. mirror images
i. rotation of the polarized light beam
j. optical isomers: laboratory synthesis vs. biosynthesis
k. racemization and dating of fossils

WATCH THE PROGRAM



AFTER WATCHING



SHAPES OF MOLECULES

a. Covalent bonding and geometry

The covalent bond is special; it has a directional character. Around any particular atom, the covalent bonds are formed in certain definite directions and not in others. As a consequence, molecules have definite shapes. We use the phrase "molecular architecture" as a general term for this spatial arrangement of atoms in molecules.

b. Methane and ethane

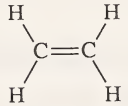
When a carbon atom is bonded to four other atoms or groups of atoms, the arrangement of the bonds around the carbon atom is tetrahedral. This is exemplified in which has four hydrogen atoms attached to a carbon atom; the carbon atom is at the center of the tetrahedron, the four hydrogen atoms at the apices. Carbon has the ability to bond to other carbon atoms as well as to other kinds of atoms. If every carbon atom in a compound is bonded to four other atoms, then the compound is said to be saturated. The electron pairs composing the bond lie between the bonded atoms.

In ethane, C_2H_6, we have two carbon atoms, each of which is bonded to three hydrogen atoms; the fourth bond is between the two carbon atoms. We visualize this molecule as two overlapping tetrahedra with each carbon atom occupying a corner of the other's tetrahedron. Rotation is permitted around this bond. Thus, the three hydrogen atoms attached to one carbon atom may have any orientation relative to the three hydrogen atoms on the other carbon atom. Long chain carbon compounds can be visualized as a chain of tetrahedra linked together.

c. Ethylene

If carbon is bonded to only three other atoms, the bonding pattern around the carbon atom is triangular. The carbon atom can be thought of as being at the center of the triangle with the three bonds directed to the corners of the triangle. Thus, the compound ethylene, C_2H_4, is visualized as two overlapping triangles lying in the same plane with each carbon atom occupying a corner of the other's triangle. The remaining corners are occupied by hydrogen atoms. Each carbon atom forms three single bonds, two to hydrogen atoms and the third to the other carbon atom. The remaining pair of electrons is used to form the second bond between the carbon

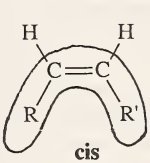
atoms. The electrons in this second bond are distributed in two clouds spread between the carbon atoms, one above and one below the plane of the molecule.



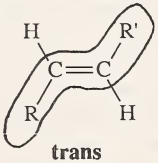
the double bond in ethylene

This second bond between the carbon atoms locks all the atoms in the molecule into one plane. Whereas in ethane, half the molecule could be rotated relative to the other half around the carbon-carbon single bond, rotation around the double bond is not allowed. To rotate the two halves of the molecule around the carbon-carbon axis would require that the second bond be broken. To break the bond would require a large amount of energy, so rotation does not occur at ordinary temperatures.

This lack of rotation and the resulting planar arrangement of the bonds around a doubly-bonded carbon atom makes **geometric isomers** possible. Suppose we replace one hydrogen on each carbon atom in the ethylene molecule by some other atom or group that we will denote by R and R'. The two isomeric possibilities are



cis



trans

If the two groups, R and R′, lie on the same side of the double bond, the compound is called **cis** (Latin for "on the same side"), while if they lie across from one another the compound is called **trans** (Latin for "across"). Because rotation is not possible around the double bond, these two compounds are distinct and have different properties.

FATS AND OILS

d. Saturated and unsaturated fats and oils

In the chemist's definition, fats and oils are the glycerol esters of saturated and unsaturated long carbon chain acids. It is for this reason that these acids are called fatty acids. (Note that this definition excludes substances that are called "oils" in everyday conversation; crude oil, motor oil, and oil of wintergreen are not "oils" in the sense of this chemical definition.) The definition includes animal fats and oils, such things as suet, lard, butter, whale oil, and vegetable fats and oils such as cocoa butter, palm oil, corn oil, olive oil, soybean oil, etc. The distinction between fats and oils is made on two levels. On the macroscopic level, fats are solids while oils are

liquids. On the molecular level, the fats are esters of either straight chain saturated acids or trans unsaturated acids. The oils are esters of cis unsaturated acids. The cis acids have a kink in the chain; they do not stack neatly, and therefore do not easily form a solid.

e. Models of saturated and unsaturated fatty acids

The space-filling models shown by John Kinsella, the food chemist, are of stearic acid (the saturated acid, the acid with the straight chain) and of oleic acid (the cis unsaturated acid, the acid with the bent chain). Stearic acid and oleic acid both have an 18-carbon-atom chain and differ only in that oleic acid has a double bond connecting the ninth and tenth carbon atoms. Because of the presence of the double bond, oleic acid has two fewer atoms of hydrogen than does stearic acid.

f. Hydrogenation of a vegetable oil

In this demonstration, Don Showalter passes gaseous hydrogen through soybean oil which has some metallic palladium suspended in it. The palladium used in this experiment is in the form of a finely divided black powder. When a hydrogen molecule, H_2, sits down on a palladium surface, it breaks into two hydrogen atoms; these hydrogen atoms can add to a double bond if an unsaturated molecule comes close. This converts the bent unsaturated chain to a straight saturated chain. The bent chains in the molecule of soybean oil are converted to straight chains. This molecule with the straight chains can stack neatly with others to form a solid. If all the molecules in the oil were hydrogenated, the result would be a very hard fat like suet. The hydrogenation is stopped before that, so that a semisolid material like margarine or shortening is produced. This semisolid material is visible in the flask at the end of the demonstration.

g. Isomerization of unsaturated fatty acids

During the hydrogenation process, the double bond is opened. While the bond is open, rotation about the bond can bring the molecule into the trans configuration momentarily. A small fraction of these molecules form the double bond again instead of adding hydrogen to produce the saturated compound. Thus, during the hydrogenation a small amount of the trans isomer is produced.

The trans isomer is straight, much like the saturated compound. There is some opinion that the trans isomer may produce the same undesirable physiological effects that are produced by the saturated acids.

OPTICAL ISOMERS

h. Mirror images

One consequence of the tetrahedral arrangement of bonds around the carbon atom is the existence of **optical isomers** or **chirality** (from Greek, **cheir**, meaning

"hand"). Optical isomers differ from one another in the same way the right hand differs from the left hand; they are mirror images, but they cannot be superposed and therefore are not the same. This phenomenon is exhibited by any molecule containing a carbon atom to which four **different** atoms or groups of atoms are attached. The animated sequence shows two molecules, in each of which a carbon atom is attached to four different groups (four balls of different colors). The two molecules are first shown as mirror images, then three attempts are made to superpose one on the other. In each attempt, the carbon atom and the top atom are in position such that they could be superposed. Then, it is shown that in none of the three possible orientations of the molecule will all four groups be superposed. Thus, like our hands, they seem the same but, being mirror images, they are different.

three non-superimposable orientations of an asymmetric molecule

the mirror-image molecule

It can be seen that, no matter how the molecule is turned, it cannot be made to coincide with the mirror-image molecule.

i. Rotation of the polarized light beam

One of the earliest observed properties of optical isomers was their effect on a beam of plane polarized light. If ordinary light is passed through a polarizing filter, only those waves that oscillate in a plane fixed by the orientation of the filter can get through. If a second filter oriented at 90° to the first is placed in the beam, no light gets through the pair. What the first filter passes, the second filter absorbs. Next we place a flask containing a solution of one of the optical isomers of a compound between the two filters. As the polarized beam passes through the solution, the plane of polarization is rotated to a new position. Now the second polarized filter is in the wrong orientation to absorb the rotated beam, and the light comes through the second filter. Next, by rotating the second filter we can again bring it to a position in which the beam is completely absorbed.

We measure the optical rotation of the solution by measuring the angle through which the second filter must be rotated to extinguish the light. If a solution of the

same concentration of the mirror-image molecules is used, the beam is rotated through the same angle but in the opposite direction. This method of measuring the rotation of a beam of polarized light is the classical method of measuring the optical activity of substances.

j. Optical isomers: laboratory synthesis vs. biosynthesis

If we attempt to synthesize one of the mirror-image isomers in the laboratory using non-chiral starting materials, we find that nature does not favor one mirror-image isomer over another, and equal numbers of the right-handed and left-handed molecules are formed. This 50-50 mixture is called a **racemic** mixture. It does not rotate the plane of a polarized light beam, because the optical effect of each right-handed molecule is just balanced by the equal and opposite effect of a left-handed molecule.

The situation is quite different when these materials are synthesized in living organisms. The proteins and carbohydrates in organisms are built out of optically active molecules: proteins out of amino acids and carbohydrates out of sugars. The fascinating thing about this is that only amino acids of the L family are used in building proteins, while in the case of the carbohydrates only sugars belonging to the D family are used. Living organisms are very selective about this.

One effect of this selectivity is that if we feed an organism with food from the wrong family, it cannot use it. We illustrate this in the program by attempting to feed yeast on a solution of L-glucose. No fermentation occurs. When we feed it D-glucose, the fermentation goes on rapidly.

Similarly only L-morphine will alleviate pain.

In the laboratory it is possible to synthesize only one of the mirror-image isomers (rather than a racemic mixture) if a the synthesis involves one of a pair of chiral molecules.

> *NOTE: The designations D and L are used to make the structural distinction between the two families of optically active materials.*

k. Racemization and the dating of fossils

In any living organism, the protein portion is built exclusively from L-amino acids. Once the organism dies, the protein begins to decay and may break down into the constituent amino acids. These are all L-amino acids. However, once the organism is dead, there is a natural tendency for the L-amino acids to racemize. If there is a low energy chemical pathway available to convert the L form to the D form, this conversion (racemization) will go on. It turns out that this racemization is very slow, requiring time intervals of the order of geologic times.

Suppose at a certain time we have a sample of a pure L-amino acid. It rotates a beam of plane polarized light by a certain amount. The sample begins to racemize.

At a later time the sample does not rotate the beam of polarized light by as much as it did before, since some D molecules have been formed. By measuring the rotation of the light beam and knowing the rate of racemization, we can calculate the length of time that has passed since the racemization began. In this way, Ed Hare is attempting to measure the age of fossils.

HANDS ON

1. *Make a list of five items in your household that are chiral and another list of five items (this must be easy!) that are not chiral. How do you decide which items are chiral and which are not?*

2. *Using two pairs of Polaroid sunglasses, look at a light source. Rotate one pair while holding the other pair fixed. Note the difference in the intensity of the light.*

3. *The light reflected from a pavement or from the surface of a pool of water is polarized. Note the difference in intensity of the reflected light with and without polarizing sunglasses.*

QUESTIONS

1. *From Column II choose the substance which is an isomer of the substance in Column I. Write "None" if there is no isomer in Column II.*

Column I	Column II
a) NH_4CNO	i) CH_3COCH_3
b) CH_3COOH	ii) $CH_2=CBr_2$
c) $HBrC=CHBr$	iii) $(NH_4)_2CO_3$
d) CH_3CH_2OH	iv) CH_3CH_2OH
e) CH_3OCH_3	v) CH_3CSSH
	vi) NH_2CONH_2

2. **Saturated** *hydrocarbons can be converted into* **unsaturated** *hydrocarbons by a process that:*

   a. removes some hydrogen atoms from the hydrocarbon molecules.

   b. removes sulfur and sulfur compounds from the petroleum.

   c. bonds additional carbon atoms to the already existing saturated hydrocarbon molecules.

   d. removes carbon atoms from the already existing hydrocarbon molecules.

3. *Which one of the following statements is* **not true** *about saturated fats?*

   a. They are usually solid at room temperature.

   b. They are usually obtained from animal sources.

   c. They contain many carbon-carbon double bonds.

   d. They are not desirable as part of a low cholesterol diet.

4. *Suppose that bonds around the carbon atom were directed to the corners of a square. Could a carbon atom attached to four different groups in this way form a chiral molecule? If necessary, cut out a couple of squares of paper to prove your answer.*

UNIT 10

SIGNALS FROM WITHIN

BEFORE WATCHING

YOU ALREADY KNOW

Covalent molecules have characteristic shapes.

A light beam carries energy in packages called **quanta**.

The energy of a light quantum is inversely proportional to its wavelength.

When light is absorbed the energy of the substance is raised.

When light is emitted the energy of the substance is lowered.

READ:

Chapter 5: "Molecular Structure and Spectroscopy"

OVERVIEW

This program illustrates the principles involved in the interaction of radiation with matter. It provides several examples of applications of spectroscopy to practical problems.

When we think of the spectrum, the first image that comes to our minds is the visible spectrum produced by a prism that spreads out white light into its component colors from violet to red. The visible spectrum covers only a small range of the entire electromagnetic spectrum. The chemist is interested in the entire range of the spectrum from gamma rays to radio waves.

Associated with each wavelength in the spectrum is a light quantum (package) that carries a particular amount of energy; an x-ray quantum has an extremely high energy, while a radio wave quantum has a very low energy. We "see" visible light simply because the energies of the chemical reactions that result in vision are the same as the energies associated with the wavelengths of light in the visible region of the spectrum.

An application of spectroscopy in the design of sunscreen lotions is presented.

The ways a molecule can possess energy are described. Every molecule absorbs different wavelengths of light. The intensity of the light transmitted by a substance is measured using a **spectrometer**. The spectrometer, in quite general terms, consists of a source of radiation, a device to disperse the light into its component wavelengths, a cell to hold the sample of material under study, and a device to measure the intensity of the transmitted beam. The light path is sketched below:

Source ⟶ dispersing device ⟶ sample cell ⟶ detector ⟶ recorder

The instrument can be programmed to change the wavelength of light passing through the cell; thus, the detector measures the intensity of the transmitted beam as a function of the wavelength. This information is recorded as a pattern. This pattern is different for every molecule; it is as distinctive as a fingerprint.

A simple example of how absorption in the visible leaves a dark space in the wavelength region of the absorbed light is shown. Finally, a series of examples of the use of infrared spectroscopy in the identification of drugs and pheromones is shown.

WHAT TO LOOK FOR:

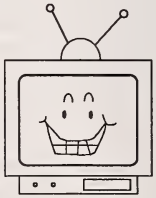
THE ELECTROMAGNETIC SPECTRUM

a. regions of the spectrum
b. energy variation in the spectrum
c. sunscreens

ABSORPTION OF RADIATION

d. ways in which a molecule can possess energy
e. an analogy to sound waves
f. chlorophyll
g. infrared spectra used to identify compounds

WATCH THE PROGRAM



AFTER WATCHING

THE ELECTROMAGNETIC SPECTRUM

a. Regions of the spectrum

Isaac Newton found that a glass prism spreads white light into its component colors. The wavelengths of visible light range from about 400 nm for violet light to about 800 nm for red light.

It was about a century later that infrared radiation was first detected in the region beyond the red end of the spectrum. Later yet, ultraviolet radiation was detected in the region beyond the violet end of the spectrum. Over the years we have learned that the electromagnetic spectrum is not limited to any specific region of wavelengths but is a continuum. Our ability to observe the spectrum is limited only by our ingenuity in devising methods of detecting the radiation in a particular region of wavelengths. The chemist is interested in all the known regions of the spectrum from gamma rays to radiowaves.

b. Energy variation in the spectrum

In Program 6 we learned that the energy of a beam of light is carried in small packages called **quanta**. The energy of a light quantum is inversely proportional to its wave length. This means that a quantum of violet light (wavelength about 400 nm) has more energy than a quantum of red light (wavelength about 800 nm). Thus, the energy associated with the spectrum is very high for gamma rays and decreases as we move to x-rays, the ultraviolet, visible, infrared, microwave, and radiowave regions. The energy of a quantum of radiation in the radio region, for example, is roughly ten million times smaller than the energy of a quantum in the visible region.

c. Sunscreens

The design of sunscreen lotions is an application of our knowledge about the ways in which light is absorbed. By choosing molecules that will absorb ultraviolet radiation in the region that is most damaging to the skin, we can protect the sunbather from sunburn. The compound, para-aminobenzoic acid (PABA for short), is one that has been found to be effective for this purpose.

It is worth mentioning that ozone is an important natural sunscreen. It filters out essentially all the solar radiation with wavelengths less than 290 nm. PABA absorbs significantly in the region from 330 to 290 nm, and so offers some protection in a

region of the ultra-violet where ozone does not. (There is more about ozone in Program 17.)

ABSORPTION OF RADIATION

d. Ways in which a molecule can possess energy

In any molecule with more than two atoms, all the nuclei and all the electrons are moving relative to each other in a complicated way. There is an energy associated with every kind of motion in the molecule. Furthermore, **there is a set of energy levels associated with every kind of motion in the molecule.** The challenge is to analyze the complicated motion in the molecule in terms of simpler motions of the nuclei and electrons. It turns out that this is not too difficult to do. There are definite types of motion that contribute to the overall motions in any molecular system. These are:

i) Translational motion

ii) The motions of the electrons in the molecule

iii) The rotation of the molecule as a whole

iv) The vibrations of the nuclei in the molecule relative to one another

i) The translational motion is simply the overall motion of the entire molecule in one direction or another. The translational motion is described by saying how fast the molecule is moving and in what direction. This kind of motion does not tell us anything about the structure of the molecule and is not interesting as far as the spectrum of the molecule is concerned.

ii) The absorption and emission of light by an electron in an atom was described in Program 6. Remember the cloud changing shape? Just as they do in the atom, the electronic motions in a molecule have a set of electronic energy levels associated with them. If light of the proper wavelength falls on the molecule, an electron can be moved to a higher energy level and the light will be absorbed; just as it did in the atom the shape of the electron cloud in the molecule will be changed. The frequencies required to move the molecule's electrons from one level to another lie in the spectral region from x-rays through the ultraviolet to the visible. The magnificent colors of all the various dyes mentioned in Program 2 are due to the absorption of light by the electrons in the dye molecules. As always, the particular frequencies that are absorbed are different for each molecule and therefore we can use them to distinguish between different molecules.

iii) The rotational motion of the molecule can be imagined roughly in the following way. Suppose we push a pin through the center of the molecule and then, using the pin as an axle, we spin the molecule like a top. For any molecule there is a set of energy levels associated with this rotational motion. The energy dif-

ferences associated with a change from one rotational energy level to another are very small compared to those between the electronic levels. Thus, the wavelengths absorbed are very much longer than those in the visible region. The rotational spectrum lies in the microwave region of wavelengths. Again, the energy levels are characteristic of the molecule. The microwave spectrum is particularly suited for studying small molecules such as water, ammonia, sulfur dioxide, and the nitrogen oxides. In the program, the rotational motion of the water molecule is illustrated by an animated drawing.

The microwave ovens that are so popular are tuned to the rotational frequency of the water molecule. As the water molecules absorb the microwave radiation they start to spin faster and faster. As these fast spinning molecules bang into the molecules surrounding them the rotational energy is dissipated into heat energy; the food gets hot.

iv) The simplest example of the vibrational motion in a molecule is illustrated in the program by an animated drawing of a diatomic molecule. The motion is like that of two balls connected by a spring. In a polyatomic molecule there are many balls and many springs, so the motion is complicated. In spite of the complication, the vibrational motion can be sorted out into simpler components. Each of these component motions has a set of energy levels associated with it. The energy differences between these energy levels is also much smaller than the differences between the electronic levels, but not so small as the differences between the rotational levels. Hence the wavelengths absorbed lie in the infrared region between the visible and the microwave regions.

It turns out that nature requires that when the energy of the vibration changes there must also be a change in the energy of rotation. As a result, the infrared spectrum consists not of lines but of sets of closely spaced lines called **bands**. There is such a **band** for each of the component vibrational motions in a molecule that vary the dipole moment of the molecule.

The infrared spectrum is one of the most useful as far as identifying a molecule is concerned. A particular grouping of atoms, such as a CH_2 group or a C=O group, in a molecule will produce a characteristic band in a particular region of the infrared spectrum. By noticing which bands are present, one can decide which groups are present in the molecule.

e. Sound waves

The demonstration with the sound generator is an example of how a macroscopic body can absorb sound energy and convert it into an organized motion of the body if the frequency is adjusted appropriately. Any large body has resonant frequencies; a bell, for example, produces a definite tone when struck by the clapper.

Conversely, if a sound wave of the same frequency as the bell tone impinges on the bell, the energy of the sound wave will be absorbed by the bell and the bell will start to vibrate. As the sound wave continues, more and more energy is absorbed, and the amplitude of the vibration of the bell gets larger and larger; ultimately the bell could be torn apart. As a practical matter, it is not easy to break a bell of any size by this method, but, as the demonstration shows, it only takes a few moments before the fragile glass beaker is shattered by the sound wave. Frequencies other than the resonant frequency are damped out and converted into thermal energy. The bell or the beaker simply gets a little warmer.

Analogically, if the proper frequency of light hits a molecule, the energy of the light will be absorbed, and an organized motion of the electrons and nuclei composing the molecule will be induced.

f. Chlorophyll

The green color of chlorophyll is a consequence of the absorption of other colors in the spectrum, predominantly those in the yellow-orange region. In the demonstration, white light is passed into the solution of chlorophyll, the green light comes through and other colors are absorbed. The absence of the absorbed light is most noticeable in the yellow-orange region, where a darkened area can be seen.

The absorption of this visible light is a consequence of a change in the electronic energy of the chlorophyll molecule.

g. Infrared spectra used to identify compounds

As we said above, infrared spectroscopy is a particularly useful tool for the identification of compounds. In the spectra shown in the program, the "valleys" indicate the wavelength region where absorption is taking place. Most molecules are complicated enough to have many absorption bands; even water has three. The net result is that the infra-red spectrum is usually quite complex. But it is unique to the molecule, just like a fingerprint.

It is now possible to store the spectra of thousands of compounds in a computer. If we measure the spectrum of an unknown compound, such as a street drug, the computer can compare that spectrum with all the others in its memory. When the computer comes up with a match, we ordinarily have a positive identification of the compound.

If the computer cannot match the unknown compound with one in its library, we can identify some of the features in the spectrum with characteristic groups of atoms. Often this is not sufficient to determine the structure of the molecule uniquely. Evidence from other measurements must be brought to bear on the problem. When the structure is finally determined, we have another spectrum to file in our library.

HANDS ON

1. *Take notice of the colors of soft drinks, or wines, or liquid food flavors, or food colors. Some of these colors seem more pure and brilliant than others; these often contain only one colored compound. Liquids that are more "muddy" in appearance often contain more than one colored compound. Caramel contains a number of colored compounds; when used as a flavoring, it often dulls the color of a soft drink.*

QUESTIONS

1. *Of the ultraviolet, visible, and infrared regions of the spectrum, which has the quanta of highest energy? Which has the quanta of lowest energy?*

2. *The phrase "quantum jump" has come into everyday use. What does the phrase mean and what is its relation, if any, to the physics of spectroscopy?*

3. *Mercury vapor emits a bright green light when an electric discharge is passed through it. How can one decide whether this light consists of one wavelength or of several wavelengths?*

4. *What kind of molecular motion changes its energy when a substance absorbs microwave radiation?*

5. *What kind of molecular motion changes its energy when a substance absorbs ultraviolet light?*

UNIT 11

THE MOLE

BEFORE WATCHING

YOU ALREADY KNOW

Elements react to form compounds.

A molecule of a compound consists of fixed numbers of atoms of the various elements in it.

READ:

Chapter 2: "The Language of Chemistry"

Chapter 6: "Weight Relationships in Chemical Reactions"

OVERVIEW

This program introduces the definition of the **mole**, the chemists' unit of measure. It reminds us that elements react to form compounds on the basis of integral ratios of numbers of atoms. When we do a synthesis, we have to bring together the proper numbers of atoms of the different elements.

Similarly, when an intravenous solution (IV solution) is prepared, it is essential that the proper **numbers of molecules** of glucose and the proper **numbers of sodium and chloride ions** be present in a given volume of solution. The osmotic properties of the solution depend on the relative numbers of the various molecules and ions in the solution.

Defining the mole and knowing the relative masses of the various atoms is simply a way to count atoms and molecules by weighing them.

The industrial story about making a polymer illustrates the importance of having the correct ratio of moles of the two reacting substances. If the ratio is not correct, the yield of product drops off drastically.

WHAT TO LOOK FOR:

HISTORICAL BACKGROUND

a. chemistry done with gases

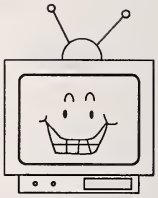
BREAKTHROUGH

b. Avogadro
c. atomic masses
d. example of the coins
e. magnitude of the Avogadro number

APPLICATIONS

f. manufacture of IV solutions
g. blowing balloons with moles of hydrogen
h. making an epoxy resin example

WATCH THE PROGRAM



AFTER WATCHING

HISTORICAL BACKGROUND

a. Chemistry done with gases

At the end of the eighteenth century, just as Dalton's atomic theory was proposed, there was a large amount of chemical experimentation being done with gases. Lavoisier describes a device for collecting samples of gases given off in chemical reactions and states that this device is one of the most important pieces of equipment in the laboratory. Having collected the gases, the chemists of that time then examined their chemical properties.

The results of these experiments were often expressed quantitatively in terms of the combining volumes of the gases; it was understood that all the volumes were measured at the same temperature and pressure. The results were often puzzling. For example, one volume of hydrogen reacted with one volume of chlorine to form two volumes of hydrogen chloride. Two volumes of hydrogen reacted with one volume of oxygen to form two volumes of water vapor. But out of this came the so-called law of combining volumes: when gases take part in a chemical change the volumes of the reacting gases and those of the products, if gaseous, are in the ratio of small whole numbers.

BREAKTHROUGH

b. Avogadro

Even after the proposal of the atomic theory by Dalton, the law of combining volumes did not appear to make sense. In 1811 Amadeo Avogadro, an Italian physicist, made a proposal that could explain the law of combining volumes. Regrettably Avogadro's view was not generally accepted until nearly 50 years later and as a consequence much confusion reigned in chemistry during that intervening period. Avogadro's hypothesis was this: that equal volumes of gases (again measured under the same pressure and temperature) contain the same number of molecules of a substance. The molecule was defined as the smallest portion of any substance that retains the chemical identity of the substance. Thus, according to Avogadro, one litre of hydrogen contains the same number of molecules as one litre of chlorine, and so on.

But this still does not explain the combining volume law for hydrogen and chlorine. Suppose we have a volume of hydrogen that contains 5 molecules of hydrogen and the same volume of chlorine that contains five molecules of chlorine. When they react, experiment shows that **two** volumes of hydrogen chloride are formed, which means we should get **ten** molecules of hydrogen chloride. If the molecules of hydrogen and chlorine consist of one atom of hydrogen and chlorine then we should have

1 atom H plus 1 atom Cl to produce one molecule HCl

This implies that one volume of hydrogen would react with one volume of chlorine to produce one volume of hydrogen chloride. The experiment says two volumes of HCl are produced. Avogadro overcame this objection by saying that if we assume that the molecule of hydrogen has two atoms in it (written H_2) and that of chlorine has two atoms in it (written Cl_2) then the experimental result is explained.

1 molecule of H_2 plus 1 molecule of Cl_2 produce two molecules of HCl. We can write this as the equation

$$\underset{\text{1 volume}}{H_2} + \underset{\text{1 volume}}{Cl_2} \longrightarrow \underset{\text{2 volumes}}{2\,HCl}$$

Note that the number of atoms of both elements is the same on both sides of the equation. **Atoms** are conserved in every chemical reaction. Mass is conserved.

c. Atomic masses

The Avogadro hypothesis (today we call it Avogadro's law) was a great step forward. John Dalton postulated that all matter was made up of large numbers of extremely tiny atoms and that each kind of atom had a characteristic mass, but there is nothing in Dalton's formulation that enables us to find out how many atoms there are in a given sample of matter. Avogadro's law moves us a big step in this direction. At least if we take the same volume of two different gases we know that these two samples of matter contain the **same** number of molecules. If we weigh the two samples of gas we obtain the relative masses of the different molecules.

For example, one litre of chlorine at 1 atmosphere pressure and 25 °C weighs 2.861 grams. Under the same conditions one litre of hydrogen weighs 0.0807 grams. The mass of the chorine molecule relative to the mass of the hydrogen molecule is

2.861 grams/0.0807 grams = 35.5

So the chlorine molecule is 35.5 times more massive than is the hydrogen molecule.

d. Example of the coins

In the demonstration, Don Showalter weighs one penny and one quarter and finds that the quarter is 2.2 times heavier than the penny; then he weighs 20 of each and obtains the same result, a quarter is 2.2 times heavier than a penny. Clearly, we don't even have to know how many we are weighing as long as we are weighing **the same number** of each.

We dealt with the same number of molecules when we used the one litre of hydrogen and one litre of chlorine; we do not need to know how many molecules are in the one litre of gas. We only need to know that it is **the same number** for both gases.

Investigation soon showed that hydrogen was the lightest element known, so the molar masses of other gases relative to hydrogen were tabulated. Then after many painstaking experiments and much debate over chemical formulas of compounds, the molar masses of nongaseous substances were determined. The values obtained by one method were often not consistent with those obtained by another method. Only after Avogadro's hypothesis was resurrected by Cannizzaro in 1859 and generally accepted soon after that was it possible to construct a consistent table of atomic masses for the elements.

e. Value of the Avogadro number

It was near the end of the 19th century before the first estimates of the value of the Avogadro number were obtained. The modern value for this constant is

$$N_A = 6.02 \times 10^{23}$$

This is the number of molecules in what we call one **mole** of any substance. This incredibly large number is the unit by which the chemist measures the amount of substance in any sample. We could never begin to count such a fantastically large number of atoms. But we can weigh the material. So we count the number of moles by weighing.

Thus, one mole of hydrogen gas contains 6.02×10^{23} molecules of H_2. The mass of this amount of hydrogen is only 2.0 grams. One mole of carbon weighs 12 grams, one mole of copper weighs 63.5 grams.

Note the drawing of the sand covering the city of Los Angeles. In respect to area, Los Angeles is one of the world's largest cities. An Avogadro number of sand particles would bury the entire city under 600 metres of sand.

APPLICATIONS

f. Manufacture of IV solutions

In the manufacture of intravenous solutions (IV solutions) it is essential that the concentration of the solutes, salt and sugar in the example shown in the program,

be correct. If the solution is too concentrated, the cells in the body will lose water to the solution and shrink to the point that they cannot function. If the solution is too dilute, water will pass from the solution into the cell. The cell will become turgid and possibly rupture. Thus, if the concentration is not correct the IV solution can possibly be lethal when it is injected. The phenomenon that governs the passage of water back and forth is called osmotic pressure. The osmotic pressure of any solution is determined by the number of solute molecules or ions relative to the number of solvent molecules. Thus, we can compose the solution intelligently only if we know how to translate masses into numbers of molecules and vice versa. This is done using the mole concept and a knowledge of the molar masses of the substances in the solution.

g. Blowing balloons with moles of hydrogen

In the demonstration with magnesium and hydrochloric acid we see that the amount of product (the hydrogen) formed does not always increase as the amount of one reactant goes up. Each of the three flasks contains one-tenth of a mole of hydrochloric acid. The amounts of magnesium are, from left to right: 0.1 mole, 0.05 mole, and 0.025 mole. In the first flask, there is magnesium left over after the reaction stops, so we may assume that the reaction stopped when the hydrochloric acid was used up. In the second flask, the same amount of hydrogen was produced, so we conclude that the hydrochloric acid was again used up. But this time the magnesium was also used up; so we may conclude that in this second flask the magnesium and hydrochloric acid were mixed in chemically equivalent amounts. This means that 0.05 mole of magnesium will react exactly with 0.1 mole of HCl. As chemists, we symbolize this 1 for 2 ratio by writing the chemical equation:

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

When no multiplier appears before any formula in a chemical equation a "1" is understood. This equation says that 1 mole of magnesium reacts with 2 moles of hydrochloric acid to form one mole of magnesium chloride and one mole of hydrogen gas. In the third flask, not enough magnesium was put in to use up the hydrochloric acid; in fact, only half as much as would be necessary. Consequently, only half the amount of hydrogen was produced.

Note that the multipliers standing in front of the formulas in any chemical equation have been adjusted so that there will be the same number of atoms of each kind on both sides of the equation. This process is called "balancing the equation". Atoms are conserved in every chemical reaction. For this reason, the equation is also an expression of the conservation of mass. An example of balancing an equation: We consider the decomposition of potassium chlorate

into potassium chloride and oxygen. Step 1. Write the correct formulas for all substances involved.

$$KClO_3 \longrightarrow KCl + O_2$$

Potassium and chlorine atoms are balanced, but on the left there are three atoms of oxygen and on the right only 2. We could take refuge in mathematics and put a multiplier of 3/2 in front of the oxygen; this would accomplish the formal result. But it is customary to use only integers. No problem! Simply multiply the amount of every substance by 2. This yields the result:

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

which is the required balanced equation.

h. Making an epoxy resin

The formation of the high molecular mass polymer using the epoxy monomer and bisphenol-A is an example of the necessity of using the correct molecular ratio in producing a product. If these two substances are mixed in the ratio of one mole of epoxy monomer to one mole of bisphenol-A, a polymer of very high molecular mass is formed; if the ratio varies much from this one-to-one value the molar mass of the polymer is much lower and the product is less desirable.

In this case of the epoxy resin, the **ratio** of moles of epoxy monomer to moles of bisphenol-A is important. In the case of the IV solutions, the absolute numbers of particles in a given volume is what matters.

HANDS ON

1. *Take a handful of beans. Watching a clock, find out how many beans you can count in a minute. Using this number, find out how many years it would take you to count 6 x 10^{23} beans.*

QUESTIONS

1. *In the reaction:*

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$

a) How many moles of iron are produced?

b) How many moles of hydrogen are consumed?

c) If four moles of iron oxide were consumed, how many moles of water would be produced?

2. *Balance the equation for the combustion of methane,* CH_4*, to form carbon dioxide and water.*

3. *The molar mass of carbon is 12 g/mol. How many atoms are there in 6 grams of carbon?*

4. *The sulfur molecule has the formula* S_8*. If the molar mass of the sulfur atom is 32 g/mole what is the molar mass of the molecule? How many sulfur atoms are there in 1.5 moles of sulfur molecules.*

5. *Consider the volumes of all the following gases at 0* ^{o}C *and 1 bar pressure. Which gas has the larger volume?*

a) 1 mol of helium or 2 moles of oxygen?

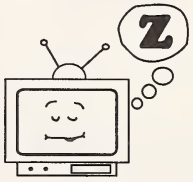
b) 32 g of helium or 32 g of oxygen?

6. *The volume of one mole of any gas at 0* ^{o}C *and 1 bar pressure is 22.7 L. What is the volume of 1 g of hydrogen under these same conditions?*

7. *There are 1000 grams of water in one litre of liquid water. If one mole of water has a mass of 18 grams, how many moles of water are there in one litre? What volume will one mole of liquid water occupy?*

UNIT 12

WATER



BEFORE WATCHING

YOU ALREADY KNOW

Ionic compounds such as NaCl.

Covalent bonds and the shapes of molecules.

Solids, liquids, and gases.

Some covalent compounds are polar.

READ

Chapter 5. "Intermolecular Forces"; "Hydrogen Bonding"; "London Forces"

Chapter 17. The whole chapter

OVERVIEW

This program looks at water, one of nature's most remarkable chemical substances. Its properties are extraordinary. Judging by its molar mass it ought to be a gas, but it is a liquid at ordinary temperatures. Liquid water has the ability to absorb large quantities of heat without its temperature changing very much. Thus, large bodies of water, lakes, rivers, oceans, are able to moderate the climate of nearby areas. The solid, ice, floats on liquid water; that's extraordinary, too. Only a few substances are known that have that property.

Water is a good solvent for many substances. For example, water dissolves the many substances that are necessary for living organisms to function.

These unusual properties are the result of the molecules of water being held to each other by **hydrogen bonds** both in the liquid and in the solid.

Although there is an enormous quantity of water on the earth, nonetheless, supplies of clean water are limited. The program concludes with a description of the challenges we face in providing clean water for all the needs in today's world.

WHAT TO LOOK FOR:

PHYSICAL PROPERTIES

a. water is a liquid at ordinary temperatures
b. water has a significant vapor pressure at ordinary temperatures

STRUCTURE

c. polarity
d. hydrogen bonding
e. density of ice and the broken bottle

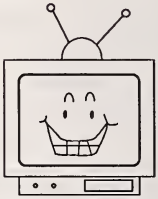
SOLVENT POWER

f. salt, alcohol, and oil

PURIFICATION OF WATER

g. contaminants in water
h. dealing with the problem

WATCH THE PROGRAM



AFTER WATCHING

PHYSICAL PROPERTIES

a. Water is a liquid at ordinary temperatures.

Everyone is so accustomed to handling liquid water that it seldom occurs to the average person to think it odd that water is a liquid. To understand the problem, we must look at the forces acting between molecules that draw them together and hold them as a liquid. We can take the boiling point as a rough measure of the strength of these attractive forces. The stronger these forces, the higher will be the boiling point of the substance.

Generally speaking, the attractive forces between molecules are proportional to the number of electrons in the molecule and to the volume over which the electrons are spread. As an example, consider the boiling points (b.p.) of the inert gases;

Element	He	Ne	Ar	Kr	Xe
b.p./°C	-269	-246	-186	153	108

The increase in boiling point is a reflection of the increasing number of electrons and increasing size of the atoms.

If we compare boiling points of the hydrides of the elements in Group VI of the periodic table we have

Compound	H_2O	H_2S	H_2Se	H_2Te
b.p./°C	100	-61.8	-42	-4

If we ignore water for a moment, in the other three compounds we see again the increase of b.p. as the number of electrons and the size of the molecule increases going from H_2S to H_2Te. We would guess that to be consistent with the trend water should boil at -100 °C. The marvelous thing is that the actual boiling point is 200 degrees higher than this predicted value. On the basis of the trend line we would predict that water would be a gas at ordinary temperatures. We will return to this point when we discuss hydrogen bonding.

b. Water has a significant vapor pressure at ordinary temperatures.

Another important property of water is that it has a noticeable vapor pressure at ordinary temperatures. This means that if we confine some liquid water in a bottle at room temperature, and shake it well, the air space in the bottle will contain a significant amount of water (2.30 mol% at 20 °C) as water vapor. If there is 2.30 mol% present at 20 °C, we say that the air is saturated, or that the relative humidity is 100%. If there is only 1.15 mol% of water vapor in the air at this temperature, we say that the relative humidity is 50%. This small amount of water vapor in the air has extraordinary importance to our comfort during hot weather. (Note: The mol% of a substance in a mixture is obtained by dividing the number of molecules of that substance by the total number of molecules present and multiplying the result by 100.)

To evaporate a liquid requires energy; when that liquid lies on our skin, the skin supplies the energy and cools as a result. If the relative humidity is 100%, then the air cannot hold any more water; if we are covered with perspiration, the perspiration cannot evaporate and we are deprived of an important cooling mechanism. Conversely, if there is no water in the air (relative humidity = 0%), the perspiration evaporates quickly and the cooling effect is immediately noticeable.

The vapor pressure of water provides a mechanism to transport water over large distances. The sun shining on the sea evaporates some water; the water vapor rises, moves over the land and may condense to form clouds. Ultimately the water falls as rain or snow. This cycle is enormously important in supplying pure water for drinking and for agriculture.

STRUCTURE

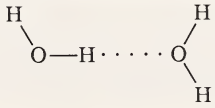
c. Polarity

The drawing in the program illustrates the tendency of the oxygen atom to attract the electrons in the bonds more strongly than the hydrogen atoms do. As a result the oxygen atom has a slight negative charge that is balanced by small positive charges on the hydrogen atoms. As a consequence, if two water molecules are brought near each other, a positive hydrogen atom on one molecule is attracted to the negative oxygen atom of the other.

A molecule with this kind of charge separation is called a **polar** molecule. The polarity of the water molecule is partially responsible for the anomalously high boiling point of water.

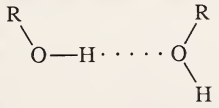
d. Hydrogen bonding

When two water molecules approach each other they can form a **hydrogen bond.** This hydrogen bond holds the two water molecules together more tightly than would the simple dipole attraction of the two molecules but not nearly so strongly as would a covalent bond. The hydrogen bond is usually denoted by a dotted line between the hydrogen atom of one molecule and the oxygen atom of the other molecule, thus:



It is the strength of these hydrogen bonds between the molecules that is responsible for the extraordinarily high boiling point of water. Each water molecule can form as many as four hydrogen bonds with neighboring molecules.

Compounds with -OH groups; such as alcohols, ROH; sugars, which have many -OH groups; and many inorganic and organic acids; also have anomalously high melting points and boiling points as a result of hydrogen bonding. In alcohols, the bonding looks like this:



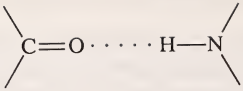
(Note: The "R" in these structures represents the rest of the molecule.)

There can also be hydrogen bonds between two nitrogen atoms in ammonia, NH_3, as well as in compounds with $-NH_2$ and =NH groups. If we compare the boiling points of the hydrides of the elements in Group V we see behavior like that in Group VI.

Compound	NH_3	PH_3	AsH_3	SbH_3	BiH_3
b.p./°C	-33.4	-87.4	-55	-17	22

The effect with nitrogen is not so large as with oxygen, but it is still quite remarkable.

The helical structure in proteins is a result of a mixed hydrogen bond between oxygen and nitrogen:



Among the elements in Group VII, fluorine exhibits hydrogen bonding in hydrogen fluoride.

e. Density of ice and the broken bottle

The curious thing about the hydrogen bond is that it can only form in particular directions. There are four electron pairs around the oxygen atom in the water molecule. We may imagine the oxygen atom at the center of a tetrahedron, then the four pairs of electrons are at the apices.

The ice structure is based on the tetrahedral arrangement of the positive and negative charges around the oxygen atom in the water molecule. Imagine the water molecule with its oxygen atom at the center of a tetrahedron and the two hydrogen atoms at two apices of the tetrahedron while two unbonded pairs of electrons are at the other two apices of the tetrahedron. Suppose that another water molecule comes up to make a hydrogen bond with the first one; for maximum interaction it must approach along one of the tetrahedral directions. As a result, the ice structure may be thought of as a collection of oxygen atoms in which every oxygen atom is surrounded tetrahedrally by four others that are hydrogen bonded to it. Three of these bonds connect the tetrahedra into pleated sheets of hexagonal rings. The fourth bond connects the sheets to make up a three-dimensional structure.

The interesting thing about this structure is that it is rather open. It has a lot of empty space in it. As a consequence it has a low density; in particular its density is lower than that of liquid water. When ice melts, the open structure collapses and the empty spaces are filled in with water molecules.

The difference in density is dramatically illustrated in the program by freezing a bottle full of water. The ice swells beyond the volume of the water and breaks the bottle.

Water is one of only a few known examples of a substance which as a solid floats on its liquid. Most solids are more efficiently packed than the liquids; there is less waste space in them, so they sink in the liquid.

SOLVENT POWER

f. Salt, alcohol, and oil.

The general rule about solubility is that "like dissolves like". In practice, this means that polar materials will be soluble in other polar materials and nonpolar materials

will be soluble in other nonpolar materials. In contrast, nonpolar materials will not dissolve in polar materials and vice versa.

The program shows examples of like dissolving like, namely the polar solvent, water, dissolving salt and alcohol, both of which are polar substances. The inability of water to dissolve oil, a nonpolar substance, is also demonstrated.

To justify the rule of "like dissolves like" we make a model. For our model of the solution process, we choose two containers; the first contains pure liquid A; the second contains pure liquid B. Now from deep inside each of these liquids we extract one molecule of each substance, then switch them so that one molecule of A is now deep inside liquid B and one molecule of B is deep inside liquid A. Next we examine the energy effect produced by this exchange.

If the attractive forces between the molecules are roughly comparable in the two liquids, then switching a molecule of A with a molecule of B will have very little net energy effect. There will be no energy barrier to the solution process. The two substances, which are "like" one another in the forces between the molecules, will dissolve in one another.

Consider the other case, in which the forces of attraction in the two pure liquids are very different. In particular, suppose A is polar, e.g. water; and suppose that B is nonpolar, oil. Now it takes a lot of energy to remove a water molecule from water, and a much smaller amount of energy to extract an oil molecule from oil. When we switch these molecules and put the oil molecule in the water and the water molecule in the oil, the forces of attraction between the "unlike" molecules are relatively weak and the energy released is very small. The net effect is that we expend a fair amount of energy to extract the molecules from the pure liquids but we do not recoup that energy when we switch the molecules and put them in the mixed liquids. Hence, a net expenditure of energy is required if the two liquids are to dissolve in one another. This energy requirement prevents them from dissolving in each other.

PURIFICATION OF WATER

g. Contaminants in water

Since water is a good solvent for many different substances, it picks up and carries many different substances as it moves through the environment. Rain water flowing over and under the ground dissolves minerals such as limestone. If there has been an "acid rain" the minerals tend to be much more soluble. When it collects in swamps, water is in contact with decaying organic matter. An uncovered chemical dump may make a nasty contribution to a flowing stream. Industrial wastes may

pour into rivers and lagoons. The falling rain collects all the contaminants of a polluted atmosphere.

h. Dealing with the problem.

Our needs for pure water are urgent. We cannot survive very long drinking polluted water. Beyond simple survival, the technologies we depend on require enormous amounts of clean water. Cattle farming requires water, agriculture requires water. Most human activities require clean water.

The methods for cleaning up any water supply must begin with reducing by as much as is feasible the flow of contaminants into that water supply. Obviously it is easier to clean something up if it isn't too dirty to begin with.

In preparing water of drinkable quality, suspended materials can be removed by filtration through a bed of sand and gravel. The water in the deep underground aquifers has been purified by passage through miles of sand and clay and rock. The microbial contamination is usually dealt with by chlorination. These two processes are the traditional ones for preparing a drinking water supply. Depending on the individual situation, other methods may be needed to remove the traces of chlorohydrocarbons and other low-level pollutants that have been observed in some water supplies.

The provision of a clean water supply presents a challenge that will require the full cooperation of government, industry, the public, and the members of the chemical profession.

HANDS ON

1. *Attempt to mix the following pairs of substances:*

solid shortening and oil;	*water and sugar.*
solid shortening and water;	*sugar and oil.*
water and vinegar;	*vinegar and oil.*

The oil in each case refers to salad oil. On the basis of your observations classify each substance as either polar or nonpolar. Remember: "like dissolves like".

QUESTIONS

1. *Neon boils at -246 °C and methane boils at -161.5 °C. Both are nonpolar and have the same number of electrons. Why the large difference in boiling point?*

2. *The boiling point of* NH_3 *is -33.4 °C while that of* CH_4 *is -161.5 °C. Why such a big difference?*

3. *Which is more soluble in water,* NH_3 *or* CH_4*? Why?*

4. *Describe three unusual properties of water. How do we account for these properties?*

5. *Which of the following will be soluble and which will be insoluble in water?*

   a) NaBr b) C_6H_6 c) C_6H_5OH d) CH_3COOH

6. *There are about 27* g of NaCl in every kilogram of seawater. How many tonnes of NaCl are there in every cubic kilometre of ocean? The density of seawater is about 1.1 g/cm^3. *1 tonne = 1000* kg.

UNIT 13

THE DRIVING FORCES

BEFORE WATCHING

YOU ALREADY KNOW

Energy changes are involved in chemical reactions.

Two atoms bonded together are lower in energy than two separated atoms.

READ:

Chapter 6. "Reactants Become Products"; "Quantitative Energy Changes in Chemical Reactions"; "Driving Forces in Chemical Reactions"; "Rates of Chemical Reactions"

OVERVIEW

This program introduces some of the basic ideas about the driving forces in chemical reactions and the factors that influence the rate of a chemical reaction.

Our observation is that Nature is unidirectional. One direction of a process we recognize as "natural"; that is, it occurs in Nature. The reverse direction is "un-natural"; it does not occur in Nature (or at least it does not occur without some outside assistance). If we put a drop of ink in a glass of water, we find that the ink slowly spreads through the entire volume of the water. If we stir the mixture, the ink spreads very rapidly throughout the volume. But no amount of stirring will result in the drop of ink separating out again. But why not?

It turns out that there are two so-called "driving forces" that determine whether or not a given transformation will occur in Nature. They are: (1) a decrease in energy and (2) an increase in disorder (entropy) on the molecular level. The combination of these two effects determines whether the transformation will go.

The situation can be reduced to a scheme:

Energy is	Disorder	Will the change occur in Nature?
released	increases	Yes
consumed	decreases	No
released	decreases	Maybe
consumed	increases	Maybe

In the last two cases, the "maybe" cases, one of the driving forces is acting in the favorable direction, the other acts in the unfavorable direction. These two driving forces can be reduced to measurable quantities, numbers with units. If the favorable driving force is larger numerically than the unfavorable one, the change will occur, at least to some extent. Otherwise, the change will not occur.

Endothermic reactions (energy is consumed) fall in the "no" and "maybe" classes in our scheme above. If we can provide the energy consumed by the reaction from an external source, that may make the reaction possible. This is the usual industrial approach to the problem.

WHAT TO LOOK FOR:

ENERGY EFFECTS IN REACTIONS

a) exothermic reactions; demonstration and graphic
b) endothermic reactions; demonstration and graphic

ENTROPY EFFECTS

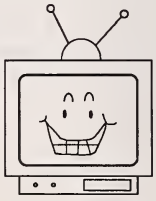
c) entropy; a second driving force
d) demonstrations of increases in disorder

INDUSTRIAL EXAMPLE

e) Union Carbide plant

RATES OF REACTION

f) setting of concrete
g) factors influencing rates of reaction
   temperature
   concentration
   catalysts
h) enzymes as catalysts
i) food preservation



WATCH THE PROGRAM

AFTER WATCHING

ENERGY EFFECTS IN REACTIONS

a) exothermic reactions; demo and graphic

Many of the common chemical reactions that we perform are exothermic, heat is released. This means that the energy of the products is less than that of the reactants. The difference in energy is the amount of energy released in the chemical reaction. In the demonstration, potassium permanganate reacts with glycerine. Sufficient heat is released so that the mixture catches fire. The potassium permanganate, $KMnO_4$, is a strong oxidizing agent, equivalent in its oxidizing power to oxygen under an enormously high pressure.

Other common exothermic reactions are:

The burning of fuels of various kinds;

Coal: $C(s) + O_2(g) \longrightarrow CO_2(g)$

Natural gas: $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

Petroleum, fuel oil, and gasoline are all hydrocarbons, like methane, CH_4, so the equations for their combustion resemble the one for the combustion of methane.

The principal constituent of wood is cellulose which can be represented by the generalized formula, $C_m(H_2O)_n$. Then, the reaction is:

Wood: $C_m(H_2O)_n(s) + mO_2(g) \longrightarrow mCO_2(g) + nH_2O(l)$

The tendency of a system to reach the lowest accessible energy state is one of the driving forces of a reaction. This tendency is often the dominant one; as a result, many, if not most, of the familiar chemical reactions are exothermic.

b) endothermic reactions; demonstration and graphic

If this tendency for the system to go to a lower energy state and release energy were the only driving force, then endothermic reactions could never occur. But they do occur. They occur in those reactions that are accompanied by an increase in **entropy**.

ENTROPY EFFECTS

c) entropy; a second driving force

Entropy is a measure of the disorderliness of a system. The tendency of a system to become more disorderly is the second driving force in natural transformations.

Consider a drop of water suspended in a vacuum. We observe that the water evaporates. Why? Since energy must be supplied to evaporate the liquid, the driving force to lower energy is pushing in the wrong direction. However, the water in the vapor state has a higher entropy than it has in the liquid state, so the driving force to higher entropy is pushing in the right direction. In this case, the tendency to increased disorder dominates and the liquid evaporates.

The most important practical rules for entropy changes are:

The entropy increases if

a liquid is formed from a solid,
a gas is formed from either a liquid or a solid,
the volume of a gas is increased,
a mixture is formed,
more molecules are formed.

Each of these rules can be understood in terms of disorderliness.

For example, a solid, in particular a crystalline solid, is a completely ordered arrangement of the constituent particles. The liquid consists of the same number of particles in about the same volume as the solid, but the particles are not arranged in an orderly pattern. So, the entropy of the liquid is greater than that of the solid. The volume of a gas is enormously greater than that of either the solid or the liquid; as a consequence, there are many more ways to arrange the particles in this huge volume and as a result there is much more disorder, a much greater entropy. For this same reason, the entropy of a gas increases with the volume.

d) demonstrations of increases in disorder

Clearly, the disorder in a mixture is greater than that in the pure substances in the same state. We recognize that when we mix a salad the natural direction of the process is to go from the segregated ingredients to the mixed salad. Once the ingredients are thoroughly mixed no amount of additional stirring or tossing will "unmix" them. Similarly, the mixing of the dye with the water is an irreversible event. We immediately recognize the "unmixing by stirring" as a television trick.

Whether or not a given transformation occurs depends on the combination of the energy effect and the entropy effect.

In any given set of circumstances, we can assign values to both effects; by adding the values we can decide whether or not the transformation can occur. We take the

example of the burning of carbon. We have expressed the effect of the two driving forces in units of R (=8.314 J/K mol) at 298 K so that the values can be added together.

energy decrease effect	entropy increase effect	sum
+158.74 R	+0.35 R	+159.09 R

If the sum is positive, then the reaction will go in Nature.

In the case of burning coal, both the energy effect and the entropy effect are positive, so the sum must be positive. Note that the energy decrease is the principal driving force in this case; the effect of the entropy increase is negligibly small.

The chemical reaction that resulted in the freezing of the beaker to the board can be written

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(s) \longrightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

There is a large increase in entropy since the reactants are both solids and therefore have a low entropy while on the right side the aqueous barium thiocyanate can move throughout the liquid phase as barium and thiocyanate ions, the ammonia molecules and the water molecules can also move throughout the liquid phase. On the product side, there are a total of 15 free particles that are free to move, whereas the particles on the reactant side are all locked tightly into the crystals. The values for the energy decrease effect and the entropy increase effect are estimated to be

energy decrease effect	entropy increase effect	sum
-24 R	+47 R	+23 R

In this case the energy decrease effect is negative (there is an energy increase). The chemical energy of the materials is increased; the energy is supplied from the thermal energy of the substances (the temperature drops and the water on the board freezes). The reaction goes only because the entropy increase overwhelms the energy effect and the net result is a positive sum.

It is instructive to look at the evaporation of water under one atmosphere pressure. The values of the driving forces at different temperatures are given in the table below.

DRIVING FORCES FOR THE VAPORIZATION OF WATER (Unit is R)

Temp/ °C	K	energy decrease effect	entropy increase effect	sum
20	293	-18.058	14.370	-3.668
60	333	-15.891	13.928	-1.963
100	373	-13.178	13.178	0.000
120	393	-12.508	12.916	+0.408

Below 100 °C the sum of the driving forces on this reaction is negative; the reaction will not go. At 1 atmosphere pressure, water does not vaporize below 100 °C, the normal boiling point. At 100 °C the sum of the driving forces is zero; this means that liquid water at this temperature and 1 atm does not tend to vaporize and also that water vapor does not tend to condense. The liquid and vapor coexist in equilibrium at this temperature and pressure; this equilibrium condition defines the boiling point. Above the boiling point the sum of the driving forces is positive, this means that water under 1 atmosphere pressure will vaporize.

While the entropy effect changes slightly with temperature, the energy effect changes quite markedly with temperature. As a driving force, the energy effect is less important and the entropy effect is more important at high temperature.

INDUSTRIAL EXAMPLE

e) Union Carbide plant.

In this large chemical plant a variety of materials are synthesized. Some of these reactions are exothermic enough so that the main driving force is the energetic one, the tendency to reach the lowest energy state. Some of the reactions are endothermic, then a choice must be made. If the endothermic reaction is accompanied by an increase in entropy, then it may be possible to reduce the effect of the energy driving force by raising the temperature; it works just like our illustration of the vaporization of water. If the required temperature is not too high, then the endothermic process becomes possible.

In some endothermic reactions it may be possible to couple that reaction chemically with a highly exothermic reaction so that the combined process is exothermic enough to overwhelm an unfavorable entropy effect.

In this particular plant we can arrange the main products on an energy ladder. The raw material, coal or petroleum, is a high energy material from which ethane is first prepared; then the ladder looks like this:

Ethane	H_3CCH_3	-84.7 kJ/mol
Ethanol	H_3CCH_2OH	-277.6 kJ/mol
Ethylene glycol	$HOCH_2CH_2OH$	-454.3 kJ/mol
Acetic acid	$H_3CCOOH + H_2O$	-555.3 kJ/mol
Oxalic acid	$HOOCCOOH + 2H_2O$	-963.4 kJ/mol
Carbon dioxide	$2CO_2 + 3H_2O$	-992.0 kJ/mol

As the values become more negative, the energy is further below the reference state. (Note: To make the energy comparison correctly, we must include the same number of hydrogen atoms (6) and carbon atoms (2) on each line as well as the compounds in which they appear.)

RATES OF REACTION

In this second part of the program, we look into the factors that influence the rates of chemical reactions. Even though a reaction can go, if the rate is too slow then the reaction will not have any practical use. If we must wait through a geologic age for the reaction to be complete, no one will use this reaction.

Example: If a mixture of oxygen and hydrogen is ignited, the mixture is converted to water within a few microseconds. An explosion occurs. However, if the mixture is left to stand without any ignition event, the reaction goes so slowly that a few billion years would be required to convert the gas mixture to water.

f) Setting of concrete

The setting of cement and concrete are important examples of a chemical reaction that is rather slow. In contrast to explosive reactions that are complete in a fraction of a second, several days are required for the setting of cement. The cement reacts with the water in the mix to form a product that bonds with the granules of cement and sand to produce a hard rock-like material. This hard material does not reach its full strength for a number of days because the chemical reaction is slow. Contractors who have prematurely removed supports from a structure being built have learned the hard way about the slow rate of the setting reaction. The program shows the

collapse of a building under construction that occurred because insufficient time was allowed for the concrete to cure.

g) Factors influencing rates of reaction.

There are three fundamental ways of changing the rate of any chemical reaction. We can change the temperature, or the concentration of one or more of the reactants, or we can add a catalyst.

- **Temperature**

Wood reacts with oxygen, burning to form carbon dioxide and water. Yet we make buildings out of wood, which remains in contact with air (oxygen) for centuries without reacting noticeably. This is a classic example of the effect of temperature. If we raise the temperature of the wood by applying a torch, the wood is soon burning rapidly. An example of this is called "flashover" by firefighters. Part of a wooden structure is ablaze, the hot gases circulate throughout the building, heating all the other parts. When a certain temperature is reached, suddenly the fire "flashes over" and the entire building is engulfed in flames.

The principal function of the water that is thrown on the flames is to cool the fire. A large amount of heat is absorbed by the vaporization of the water. When the temperature drops far enough the fire goes out.

- **Concentration**

Don Showalter's demonstration with the burning wooden splint and the bottle of oxygen is a dramatic example of the effect of concentration on the rate of reaction. Since air is only 20% oxygen, the concentration of the pure oxygen is five times greater. The rate of combustion of the wood is correspondingly greater.

- **Catalysts**

A catalyst is a substance that increases the rate of a reaction, often by an enormous factor. The demonstration of the oxidation of tartrate ion by hydrogen peroxide catalyzed by cobalt chloride shows quite clearly by the color changes that the cobalt compound participates in the reaction but at the end comes back to its original condition.

h) Enzymes as catalysts

Enzymes are the most important catalysts of all. All of the chemical reactions that go on in organisms, whether they be plant or animal, are catalyzed by enzymes; and there is an enzyme designed for every reaction.

i) Food preservation

The spoilage reactions that go on in foods are often catalyzed by enzymes. One of the tasks of the food chemist is to find ways to minimize the rates of the food spoilage reactions.

Note that the other methods of food preservation are applications of our knowledge of reaction rates.

Refrigeration and freezing lowers the rates of food spoilage reactions by lowering the temperature.

Sealing the food in vacuum reduces the concentration of oxygen and so lowers the rate of spoilage.

HANDS ON

1. *Using a pair of pliers, hold a nail in a candle flame. Observe. For comparison, hold a piece of fine steel wool in the flame. Observe. (Note: Chemically, the nail and the steel wool are the same.) The reason for the increased rate of reaction with the steel wool is the larger surface area per gram; this effectively increases the concentration. Also, the steel wool heats up more quickly than does the nail, so there is a temperature effect as well. Increasing the surface area of a solid reactant often increases the rate of reaction; for example, inflammable dusts sometimes explode in flour mills.*

2. *Next time you cut yourself and use hydrogen peroxide to cleanse the wound notice the evolution of oxygen. The decomposition of the hydrogen peroxide is catalyzed by the iron in the hemoglobin. Put a little hydrogen peroxide on a bit of rust with a drop of vinegar. The mixture of rust and vinegar produces a little bit of a soluble iron compound which catalyzes the decomposition of the peroxide. Try vinegar and peroxide alone and rust and peroxide alone. Compare the results.*

3. *Next time you use a meat tenderizer (most contain the enzyme, papain) realize that the enzyme is beginning the digestion of the protein. This predigestion makes the meat more tender.*

4. *Hold a small piece of white bread in your mouth so that the enzymes in the saliva can act on it. Note the change in taste as time passes. The starch in the bread is hydrolyzed by the enzymes to produce sugars.*

QUESTIONS

1. *What is meant by an exothermic reaction? by an endothermic reaction?*

2. *When sugar dissolves in water there is no noticeable heat effect. What is the driving force for this change?*

3. *Name three ways to increase the rate of a reaction.*

4. *Consider a new deck of cards arranged with the suits in order and each suit in numerical order. Now shuffle the deck. What driving force governs the change?*

5. *Why does freezing food retard spoilage?*

UNIT 14

MOLECULES IN ACTION

BEFORE WATCHING

YOU ALREADY KNOW

The rates of chemical reactions depend on the temperature, pressure, and concentration of the reacting species.

The rate of reaction can be increased by the addition of a catalyst.

READ:

Chapter 6. "Rates of Chemical Reaction"; "Reversibility of Chemical Reactions"; "Chemical Equilibrium"

OVERVIEW

This program points out that molecules can react only if they collide with an energy exceeding a minimum amount, the activation energy. Increasing the temperature increases the fraction of the collisions that have energies exceeding the activation energy. Addition of a catalyst lowers the activation energy and thus increases the rate of reaction. In reactions that require an initiating event such as a spark, this event introduces active species such as atoms that permit the reaction to follow a low activation energy path; in this sense, the initiating event is similar to introducing a catalyst.

Chemical reactions come to equilibrium when the rate of the forward reaction is equal to the rate of the reverse reaction. This often occurs when there are comparable amounts of both reactants and products in the closed reaction vessel. The ammonia synthesis reaction is an example. Ways to manipulate the equilibrium, using the LeChatelier Principle as a guide, so as to increase the yield of product, are described.

WHAT TO LOOK FOR:

MOLECULAR COLLISIONS

a) kinetic energy in collisions
b) animation of the collision between a hydrogen molecule and a bromine atom

ACTIVATION ENERGY

c) provision of "additional energy"
d) hydrogen balloon and the Hindenberg catastrophe
e) demo: carbon disulfide and nitric oxide
f) activation energy diagram

INDUSTRIAL EXAMPLE

g) the rhodium catalyst

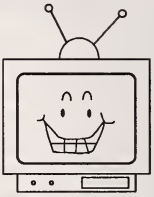
REVERSIBLE REACTIONS

h) ski lift and tank examples

THE LECHATELIER PRINCIPLE

i) the cobalt chloride example
j) the ammonia synthesis

WATCH THE PROGRAM



AFTER WATCHING

MOLECULAR COLLISIONS

a) Kinetic energy in collisions

Two molecules must be in contact with one another before they can react to produce new chemical species. But just being in contact is usually not sufficient. The collision between the two molecules must involve at least a certain minimum of energy before they can react. This minimum energy is called the **activation energy** and is different for every chemical reaction. The kinetic energy of the colliding molecules provides this energy.

b) Animation of the collision of a hydrogen molecule and a bromine atom

Any moving object possesses energy, kinetic energy, because of its motion. If two molecules are to react chemically upon collision, they must collide with more than a critical minimum energy, called the "activation energy". In a sample of gas, the molecules range in speed from very slow to very fast. So if two molecules having relatively low speeds collide, the energy involved in the collision may not be sufficient to enable them to react. On the other hand, if the speeds of the molecules are large enough so that the energy involved in the collision exceeds the activation energy, then the molecules can react.

ACTIVATION ENERGY

c) Provision of "additional energy "

Because they have different speeds, the molecules in a gas have different kinetic energies. It can be shown that the **average kinetic energy** associated with this chaotic motion in the gas is proportional to the absolute temperature of the gas (the temperature measured in kelvins). Conversely, if we raise the temperature of the gas, the average kinetic energy of the molecules increases. Therefore, the higher the temperature the greater the number of collisions that involve energies above the activation energy. It is these highly energetic collisions that produce the chemical reaction.

Thus, the increase in temperature produces a relatively large increase in the rate of the reaction. If the reaction releases heat, then the temperature increases even more

as the reaction continues. This, in turn,increases the reaction rate. If the reaction rate is great enough, the result may be a thermal explosion.

d) Hydrogen balloon and the Hindenberg catastrophe

In both of these episodes, the chemical reaction is the combination of hydrogen and oxygen to produce water:

$$2H_2O + O_2 \longrightarrow 2H_2O$$

When we say that sometimes we must provide additional energy to the reaction mixture to get the reaction to go, it does not necessarily imply that the amount of additional energy required is in proportion to the amount of materials that are to react. The two hydrogen reactions, the explosion of the balloon filled with hydrogen in the laboratory and the explosion of the Hindenberg, are a good example of this. Each of these reactions required only an **initiating event** to set off the reaction: the candle flame in contact with the hydrogen balloon in the laboratory and the spark in the case of the Hindenberg. The spark, for example, produces a few hydrogen atoms. Since a hydrogen atom has an unpaired electron it is very reactive. It can react with an oxygen molecule to produce two more species with unpaired electrons, an OH radical and an O atom.

$$H + O_2 \longrightarrow OH + O$$

These species, OH and O, are also very reactive; as a consequence, the reaction, once started, goes very rapidly and in many circumstances, explosively. In the laboratory example, the candle flame also puts highly reactive species into the reaction volume.

e) Demo: carbon disulfide and nitric oxide

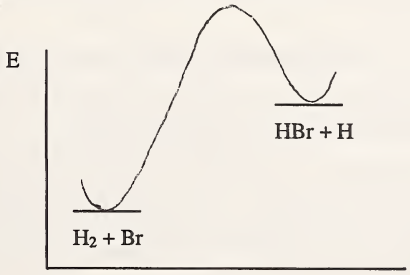
In this reaction, just as in the hydrogen-oxygen reaction, the application of a match provides an initiating event. This reaction is noticeably slower than the hydrogen-oxygen reaction; it requires several seconds for the flame to propagate downward along the tube.

f) Activation energy diagram

As two molecules approach on a collision course there is a slight attractive force acting between them when they are several molecular diameters apart; as they come in contact with each other they experience a repulsion. It requires a high energy to force them closer; this energy is supplied by the kinetic energy of the two colliding molecules. If the molecules collide hard enough and in the right configuration, the existing bonds are loosened somewhat and new bonds begin to form. In this condition, the composite of the two molecules is called an "activated complex" and

it is at the top of the energy hill. If the new bonds grow stronger and the old ones grow weaker, then this complex can fall apart to form products.

In the diagram shown in the program, the energy of a hydrogen molecule and a bromine atom, widely separated, neither of which is moving, is represented by the horizontal line at the lower left side of the graph.



The energy of the products of the reaction, an atom of hydrogen and a molecule of hydrogen bromide, is represented by the horizontal line on the upper right side of the diagram. To produce products, the system must surmount the energy hill that lies between the reactant and product states. Thus, only the molecules that collide with a kinetic energy exceeding the energy difference between the reactant state and the top of the hill can react. This energy difference is called the **activation energy** of the reaction.

As we mentioned above, raising the temperature is one way to increase the fraction of collisions that involve more energy than the activation energy. This will allow more systems to pass over the "hill" and thus increase the rate of reaction.

Another method of increasing the rate of reaction is to lower the activation energy "hill". This is what is done in the case of the hydrogen-oxygen reaction and the carbon disulfide-nitric oxide reaction. The initiating event in these cases introduces species (the hydrogen atom, for example) which provide a reaction path that has a much lower activation energy than does the simple thermal reaction. As a consequence, the reaction suddenly goes at room temperature.

Catalysts also increase the rate of reaction by providing a reaction path that has a lower activation energy than any other available path.

INDUSTRIAL EXAMPLE

g) The rhodium catalyst

The purple solution of rhodium chloride shown at the beginning of the industrial sequence of the film is the starting material for the synthesis of an organometallic

compound that serves as a catalyst for the addition of carbon monoxide to methyl acetate. The reaction is

$$CO + CH_3OCOCH_3 \longrightarrow CH_3COOCOCH_3$$

Acetic anhydride is so-called because it reacts with water to produce two molecules of acetic acid:

$$CH_3COOCOCH_3 + H_2O \longrightarrow 2CH_3COOH$$

The acetic anhydride is an important synthetic intermediate in the manufacture of aspirin as well as acetate textiles and plastics.

Two things need to be emphasized. The amount of catalyst used is relatively small and is almost all recovered. Remember the demonstration in the preceding program that showed the catalyst was unchanged at the end of the reaction. Thus, even though the catalyst may be very expensive, as in this case of the rhodium compound, so little is lost in the reaction (ideally none is lost) that it can be economic to use it. It is worth mentioning that a large fraction of the world's supply of platinum and palladium exists in the form of catalysts in the reactors of the petroleum and chemical industries.

Catalysts are widely used in industrial synthesis not only because they increase the rate of reaction but because they can be designed to increase the rate of the desired reaction without increasing the rate of competing reactions. (There will be more about catalysts in Program 20.)

REVERSIBLE REACTIONS

h) Ski lift and tank examples

Many chemical reactions do not go to completion. In a closed system, as soon as some of the products are produced they begin to react with each other to produce reactants by the simple reverse of the process by which the products were formed.

For example, consider the collision of a hydrogen molecule with a bromine atom. As the two particles collide they form an activated complex at the top of the energy hill. If we mentally freeze this complex in time, we have the situation shown in the diagram:

$$H — H — Br$$

Just looking at this arrangement without considering how it got to be there, we could say that it is a tossup whether the complex will break up to form

$$H \quad + \quad H—Br$$

or

$$H—H \quad + \quad Br$$

If it forms the HBr and the H atom, we see this as the result of the forward reaction.

On the other hand, if the same complex had been formed by the collision of an HBr molecule and an H atom and then had fallen apart to produce H-H and Br we would say that the reverse reaction had occurred.

When a transformation occurs in a single molecular act, such as the collision between the H-H molecule and Br atom, then nature requires that the reverse transformation must be possible by the exact reverse process. Thus, if we have

$$\underset{\text{(initial state)}}{H—H + Br} \longrightarrow \underset{\text{(complex)}}{H—H—Br} \longrightarrow \underset{\text{(final state)}}{H + H—Br}$$

It must be possible to have

$$\underset{\text{(final state)}}{H + H—Br} \longrightarrow \underset{\text{(complex)}}{H—H—Br} \longrightarrow \underset{\text{(initial state)}}{H—H + Br}$$

The path for the reverse reaction is simply the reverse of the path of the forward reaction. Note that this implies that if the activation energy hill is lowered by the addition of a catalyst, the hill is lowered by the same amount for the reverse reaction.

Since the rates of both reactions depends on the concentrations of the reacting materials, in the beginning the reverse rate is zero since there are no products present to react. As the concentrations of products build up, the rate of the reverse raaction gets larger. Meanwhile the concentrations of the reactants are getting smaller and the rate of the forward reaction is getting smaller. Ultimately, the rate at which products are formed is balanced by the rate at which they undergo the reverse reaction to form reactants. In this situation, we say that the reaction is in chemical equilibrium.

Two essential points must be made about this equilibrium state. First, the equilibrium is not static, but dynamic; that is, at equilibrium, the forward and reverse reactions are still going on but with no apparent net effect. Second, the equilibrium position can be shifted by altering those variables that affect the rates of reaction, e.g. temperature, pressure, and concentrations.

The analogies shown in the program, the ski lift and the two tanks, exemplify the situation.

In the ski lift analogy, the population at the top of the lift (the product state) and the population at the bottom (the reactant population) both stabilize when the rate at which the lift delivers people to the top is equal to the rate at which they depart down the slopes. For the sake of the analogy it is understood that there is no other source of people at the bottom; no buses delivering skiers, no hotels disgorging new participants, etc. (We are dealing with a closed system.)

In the analogy of the two tanks of water, the flow of water from the upper tank is rapid at the beginning but slows down as the head of water diminishes. The reverse rate, in which the water is pumped from the lower tank to the upper one, increases as the depth of water in the lower tank increases. In the first example, the rates come into balance when the upper tank is nearly empty (the reactants are nearly consumed) and the lower tank nearly full.

If we slow the rate of the forward reaction by replacing the delivery pipe with a narrower one, then the rates will come into balance before the water level in the upper tank has dropped as far as it did in the first experiment. In this case, the rates balance when the upper tank is nearly full and the lower one nearly empty. (Again, the system is closed.)

THE LECHATELIER PRINCIPLE

The LeChatelier principle states that if a system in equilibrium is disturbed, the equilibrium will shift in such a way as to counter the disturbance.

Consider the tank analogy. Assume the equilibrium state has been reached, as in the first example in which the upper tank is nearly empty. Suppose that we pour a quantity of water into the upper tank. This immediately raises the rate of flow out of the upper tank. The flow into the lower tank raises the rate of the flow through the pump back into the upper tank. A new equilibrium is established when these new rates of forward and reverse reaction come into balance. The net result is that the level of the water in the upper tank is somewhat higher than in the first equilibrium state but not as high as it was immediately after the addition of the extra water. The equilibrium shifted to counter the effect of the disturbance. One can make a similar argument to illustrate the result if extra water were added to the lower tank. Again, the equilibrium would shift in such a way as to moderate the effect of the addition. The addition of water to this system of tanks corresponds to changing the concentration of a reactive substance in a chemical reaction.

i) The cobalt chloride example

The two beakers containing cobalt complexes provide another example of the operation of the LeChatelier principle. The beaker on the left contains a water solution of cobalt chloride. In this solution the cobalt ion is hydrated; it has the formula, $Co(H_2O)_6^{2+}$. This species has a deep pink color. If the concentration of

chloride ion, Cl^-, is increased, a reaction occurs to produce the $CoCl_4^{2-}$ ion, which is blue:

$$Co(H_2O)_6^{2+} + 4Cl^- \longrightarrow CoCl_4^{2-} + 6H_2O$$

(pink) (blue)

If we start with the pink solution and add chloride ion, as Don Showalter does in the demonstration, then the pink complex is converted to the blue complex. The greater the concentration of chloride the greater will be the concentration of the chloro complex, the blue ion. Both the pink ion and the blue ion are present in both beakers, but there are relatively few of the pink ions in the blue solution and relatively few of the blue ions in the pink solution. In each solution there is a chemical equilibrium that is simply the reaction above, but now written with a double-headed arrow.

$$Co(H_2O)_6^{2+} + 4Cl^- \rightleftharpoons CoCl_4^{2-} + 6H_2O$$

(pink) (blue)

If we apply the LeChatelier principle to this equilibrium, we can see that if chloride ion is added to the pink solution the system will counter by using up chloride ion to form the blue ion. Adding chloride ion increases the rate of the forward reaction, thus consuming chloride ions.

Similarly, addition of water to the blue solution reduces the concentration of chloride ions and thus slows the rate of the forward reaction, with the result that the reverse reaction is relatively faster and, therefore, the blue ions are decomposed. Both of these effects are demonstrated in the program.

j) The ammonia synthesis

Ammonia is one of the most important industrial products in the world. The world production of 60 million tonnes exceeds that of any other chemical except sulfuric acid. On the other hand, if we count molecules, we make more molecules of ammonia than we do of sulfuric acid. And, since each molecule of ammonia requires one and one-half molecules of hydrogen, it follows that we make more molecules of hydrogen than of any other material.

The direct synthesis of ammonia from nitrogen and hydrogen was devised by the German chemist Fritz Haber; the first plant was in operation in 1911. The reaction is

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

A double arrow is used to indicate that the forward and reverse reactions go on at comparable rates.

The ability to synthesize ammonia freed Germany of its dependence on Chilean nitrates for both explosives and fertilizer. This freedom enabled Germany to fight a war, WWI, which would otherwise have been lost within a few weeks.

The ammonia synthesis provides an instructive example of how we can manipulate a chemical equilibrium. Since both the forward and the reverse reactions go on at comparable rates, when the equilibrium is established all three substances, nitrogen, hydrogen, and ammonia, are present in the mixture. The challenge is to arrange matters so as to get as much ammonia as possible. This is done by choosing the temperature and pressure appropriately.

We begin by considering the effect of changing the temperature. The synthesis reaction is exothermic; we can symbolize the release of heat by including it in the chemical equation

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{HEAT}$$

We now try to lower the temperature by letting heat flow out. By the LeChatelier principle the system will try to counter this disturbance. It does this by shifting the reaction in the direction that will produce more heat. In this case, that means that the equilibrium position is shifted toward the right side of the reaction, more ammonia is produced. This, in turn, means that at low temperatures we will get more of the desired product, ammonia, than at high temperatures. But at low temperatures the reaction is so slow that, effectively, we do not get any ammonia at all. So the temperature is increased, but no more than is necessary to give a reasonable reaction rate.

The other adjustable parameter is the pressure. Note that there are three moles of gases on the reactant side of the equation and two moles of gas on the product side. If we attempt to increase the pressure, the LeChatelier principle says that the system will try to reduce this disturbance. It does this by shifting the equilibrium in such a way as to reduce the volume the system occupies. The system will occupy less volume if it has fewer gas molecules; thus, the equilibrium will shift to the product side. The increase in pressure increases the yield of ammonia.

Finally, if some of the ammonia is removed from the reaction mixture, the reaction will counter that disturbance by synthesizing more ammonia.

All of these tricks are used to get as much ammonia as possible from the reaction.

HANDS ON

1. *Add a teaspoon of vinegar to a cup of water; mix thoroughly. Call this mixture 1. Take one teaspoon of mixture 1 and add it to a cup of water. Call this mixture 2. Divide each mixture into two portions. To one of the portions of mixture 1 and mixture 2 add a teaspoon of baking soda. Note the difference in the rate of reaction. Heat the other portions of mixture 1 and mixture 2. Add a teaspoon of baking soda to each. Note the difference in the rate of reaction between the hot and cold portions of the two mixtures.*

QUESTIONS

1. *What is meant by the activation energy of a reaction?*

2. *(a) What does a catalyst do?*

   (b) How does a catalyst do it?

3. *Consider the reaction*

$$3O_2(\text{gas}) + \text{HEAT} \rightleftharpoons 2O_3(\text{gas})$$

Suppose this reaction involving oxygen and ozone comes to equilibrium. What effect will each of the following changes have on the amount of ozone present at equilbrium?

(a) an increase in temperature	*More*	*Less*	*No change*
(b) a decrease in pressure	*More*	*Less*	*No change*
(c) addition of O_2 molecules	*More*	*Less*	*No change*

4. *(a) How does a catalyst affect the rate of a reaction such as the ammonia synthesis?*

   (b) How does a catalyst affect the amount of ammonia present at equilibrium?

5. *In a sealed vessel containing only water, the following change in state comes to equilbrium (the process is endothermic going from left to right):*

$$H_2O(\text{liquid}) + \text{HEAT} \rightleftharpoons H_2O(\text{gas})$$

   If heat is added to the system, in which direction will the equilibrium shift?

UNIT 15

THE BUSY ELECTRON

BEFORE WATCHING

YOU ALREADY KNOW

Energy is conserved.

There are different sources of energy, such as: oil, coal, natural gas, nuclear, solar, geothermal wells, ocean currents, garbage, etc.

What exothermic and endothermic reactions are.

READ

Chapter 10: "Oxidation-reduction defined from the electron point of view"; "Reduction--the opposite of oxidation"; "Electrolysis"; "Batteries"

OVERVIEW

This program deals with oxidation and reduction, the loss and gain of electrons. The two processes go together since if something loses electrons, something else must gain electrons. Although the oxidation-reduction process is very general, here we deal only with metals.

When a metal oxidizes, it corrodes. The corrosion of iron is one of the common processes that goes on. Any place where there is a bit of iron or steel, some moisture, and some oxygen, the metal will corrode. The pitting corrosion in boilers is an example.

Looking at the bright side, in principle, we can take any corrosion process and harness the energy released in an electrochemical cell to produce electrical power . Unfortunately, that is not always practical. However, the zinc-copper sulfate reaction is a reaction that **can** be harnessed to produce electrical power. Metallic zinc reacts with copper sulfate to produce zinc sulfate and metallic copper. The active metal, zinc, corrodes. In the program, we show the reaction and then the corresponding reaction in the traditional telegrapher's cell. The lithium cell, used

in the heart pacemaker, is another example; in this case, the lithium metal corrodes. The lead storage cell, since it is rechargeable, provides a slightly different example of a power-producing device.

Finally, instead of taking electrical power from a chemical system, if we put electrical power into a system, we can produce high energy substances. This process is called electrolysis. The decomposition of water to yield hydrogen and oxygen, the electrolysis of bauxite to produce aluminum, and the recharging of the lead storage cell are examples.

WHAT TO LOOK FOR

MACROSCOPIC PHENOMENA

a. definitions of oxidation and reduction
b. the physical appearance of various kinds of corrosion products
c. demonstration of the reaction of metallic zinc with copper sulfate solution

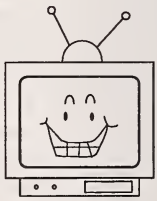
CELLS

d. demonstration of the zinc-copper electrochemical cell
e. the lithium cell
f. the lead storage battery

ELECTROLYSIS

g. to decompose water
h. to manufacture aluminum
i. to recharge a battery

WATCH THE PROGRAM



AFTER WATCHING

MACROSCOPIC PHENOMENA

a. Definitions of oxidation and reduction

Note first the definition of oxidation as a loss of electrons and reduction as a gain of electrons. These are the most widely usable definitions of oxidation and reduction.

b. The physical appearance of various kinds of corrosion products

The program begins with a montage of shots showing the corrosion of metals, mainly iron. Pieces of heavy machinery have been left out in a junkyard and allowed to rust away.

Note particularly the thick, rather heavy, rough appearance of the rust coating on these objects. Heavy flakes of rust appear on iron objects; these flakes are only loosely attached to the iron and soon fall off, exposing new iron surface which can be further corroded.

Contrast the appearance of the rough, heavy, flaky coat of rust on iron with the appearance of the corrosion coat on the bronze bell shown in the program. The coat on the bell is smooth and adheres tightly to the metal underneath. Because this coat adheres to the metal, it protects the metal from further attack. The coating is said to be "protective". In the case of copper, the green coating is called **patina**, and its composition is modified from that of a simple oxide by the presence of moisture and sulfur oxides in the air. Depending on the location, the patina may be a basic copper sulfate, $Cu(OH)_2 \cdot CuSO_4$, or in coastal areas a basic copper chloride, $[Cu(OH)_2]_3 \cdot CuCl_2$.

The oxide coating on aluminum is also protective. In this case, the coating is so thin (it is only a couple of hundred atoms thick) that you can't see it. It is evidenced only by a very slight dulling of the shine on an aluminum article. This thin, adherent coat of aluminum oxide is not dissolved or otherwise affected by the moisture in air; in addition, it prevents any further attack on the metal by the oxygen in the air. Consequently, in spite of the fact that aluminum is a very active metal, we can use it for many everyday applications. The same is true of magnesium and magnesium-aluminum alloys.

In **the Kelley interview**, notice the deep pits in the corroded pipe. Because pitting removes a lot of metal from a small area, the piece will fail much sooner than if the attack were uniformly distributed over the surface.

Note in passing: Corrosion occurs more rapidly in a marine atmosphere, where there is salt in the moist air. We will return to this point later.

c. Demonstration of the reaction of metallic zinc with copper sulfate solution

In the demonstration showing the reaction of metallic zinc with copper sulfate, note that the reaction consists of two processes:

The loss of electrons by a zinc atom:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The two electrons are gained by a copper ion, which is reduced to a metallic copper atom:

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Heat is released in this chemical reaction; it is this energy that can be recovered as electrical energy if the reaction is done in an electrochemical cell.

CELLS

d. Demonstration of the zinc-copper electrochemical cell

Realize that after the zinc ion leaves the zinc metal plate, the electrons are available at any location on the zinc plate. In general, the copper atom will be formed at a position some distance away from where the zinc atom dissolved. This is important because it enables us to use this reaction to construct an electrochemical cell, the copper-zinc cell demonstrated by Don Showalter a little later on in the film.

An electrochemical cell is a device that can convert the energy in chemical substances to electrical energy.

The word "battery" originally meant a group of several electrochemical cells connected together to produce a concerted electrical effect. For example, the 12 volt car battery consists of six 2 volt cells connected together; the common 9 volt battery used in smoke detectors consists of six 1.5 volt cells connnected together. Today, the word "battery" is commonly used for any electrochemical device that produces power, whether it be a single cell or several cells connected together. Thus, a single dry cell is often called a battery. The usual flashlight "batteries" are, in fact, single cells with a voltage of 1.5 volts.

The voltage of electrochemical cells:

The voltage of a cell is a measure of the combined driving force (includes both energy and entropy) of the chemical reaction that goes on in the cell. The greater the driving force of the chemical reaction, the greater the voltage of the cell.

e. The lithium cell

Most chemical reactions that are of practical importance for electrochemical cells yield cells with voltages in the range from 1 to 1.5 volts. For example, the zinc-copper cell, the Daniell cell, demonstrated in the film has a voltage of about 1.1 volts. Occasionally, higher voltages are obtained. For example, 2 volts in the lead storage cell, and 3.4 volts in the lithium cell. This very high voltage in the lithium cell follows from the fact that lithium is a very active metal and loses electrons very easily. The driving force for the electrochemical reaction is consequently very large.

In the discussion of the lithium battery notice the chart that shows the cell voltage on the vertical axis. The horizontal width of the area for the lithium cell, the orange area, is six times that for the common alkaline cell. This means that the total energy obtainable from the lithium cell is six times greater that that obtainable from the alkaline cell. The useful life is about twice that of the alkaline cell.

Note on cell voltages: *The cell voltages depend on the concentrations of the electrolytes in the cell. For example, in the Daniell cell, the voltage depends on the concentrations of the zinc ions and copper ions in the solutions. Conversely, once we know that dependence, we can measure the concentrations of these ions by measuring the voltage of the cell. Thus, cells of this kind can be used as* **sensors** *to monitor the concentration of, for example, the zinc ions in a solution. By an appropriate choice of electrodes we can monitor the concentration of any substance that participates in a cell reaction.*

f. The lead storage battery

Note that in its operation, the lead storage battery produces lead sulfate on both the cathode and anode surfaces. At the cathode, solid lead dioxide gains electrons and is reduced to solid lead sulfate:

$$PbO_2(s) + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$$

At the anode, solid lead loses electrons and is oxidized to solid lead sulfate:

$$Pb(s) + SO_4^{2-} \longrightarrow PbSO_4(s) + 2e^-$$

The overall reaction is obtained by adding the reactions on each electrode:

$$Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4(s) + 2H_2O$$

Note that in producing electrical energy, the cell consumes sulfuric acid. This reduces the density of the electrolytic solution in the cell. Thus, the state of charge of the cell can be determined by measuring the density of the electrolyte.

In this chemical reaction, materials with high chemical energy are converted into materials with low chemical energy; during the transformation, 390 kJ of electrical energy is produced.

The marvellous thing about this reaction is that if we pass an electrical current (obtained from the alternator in the car) through the cell in the opposite direction, the chemical reaction is reversed and the battery is recharged. The electrical energy from the alternator is converted to chemical energy as the high energy substances, Pb, PbO_2 and H_2SO_4, are formed.

It is remarkable that the storage battery can be cycled (discharged and recharged) in this way with very little energy loss in the cycle. The energy loss in the cycle varies between 1% and 10%, depending on how rapidly the charging and discharging are done. The more rapid the rate of charge and discharge, the greater the energy loss in the cycle.

It is worth mentioning that without the lead storage battery (or a comparable device) we would not be using the high powered cars that we drive today. Before the days of the electric starting motor powered by the lead storage battery, for the most part, only men were strong enough to crank the engine by hand to get it started; and those cars had small 4 cylinder or 6 cylinder engines. Few men (if, indeed, any) could hand-crank a 375 horsepower engine in a large American car of today.

ELECTROLYSIS

Electrolysis is the second half of our story.

g. Electrolysis: to decompose water

By passing an electrical current through a chemical system, high energy substances can be synthesized. For example, when a current is passed through water (containing a little electrolyte to make it conducting), the water is broken down into its constituent elements, hydrogen and oxygen. The reactions are:

At the cathode: $4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$

At the anode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Notice that the electrodes at which these reactions occur are spatially separated from each other by about four inches. That is important, because if the reactions took place right on top of one another the hydrogen and oxygen might simply recombine (especially in the presence of the platinum electrodes) and there would be no net effect.

Electrolysis is unusual in that half of the reaction takes place at a distance from where the other half of the reaction takes place. That fact is useful in that it makes it easy to keep the new high energy products from reacting with each other. Industrially, the challenge is to keep the electrodes relatively close together, so that the equipment is compact, and therefore efficient, and still keep the high energy materials out of each other's way so that they will not react with each other.

h. Electrolysis: to manufacture aluminum

The electrolyte used in the production of aluminum is a solution of aluminum oxide in cryolite, a complex salt of aluminum, Na_3AlF_6. This molten electrolyte contains aluminum ions, Al^{3+}, and oxide ions, O^{2-}. At the carbon cathode, the aluminum ion is reduced to aluminum metal,

$$Al^{3+} + 3e^- \longrightarrow Al$$

The temperature of the cell is above the melting point of aluminum so the aluminum formed can be drawn off as a liquid.

At the anode, the oxide ion is oxidized to an oxygen atom

$$O^{2-} \longrightarrow O + 2e^-$$

Since the anode is made of carbon, the oxygen atom can react with the electrode to form carbon monoxide; this in turn can react with another atom of oxygen to form a molecule of carbon dioxide. The net result is that the gas coming off the anode is a mixture of carbon monoxide and carbon dioxide, as well as some fluorine compounds resulting from the decomposition of the cryolite. The carbon anodes are consumed in the process and must be regularly replaced.

i. Electrolysis: to recharge a battery

Recharging a battery is an example of an electrolysis reaction. Why is it that we cannot recharge any battery?

The reason is that most batteries contain some water, and, unless special conditions are fulfilled, whenever a current is passed through an aqueous solution the most likely electrolytic reaction is the decomposition of water into hydrogen and oxygen. So, if we were to try to recharge an ordinary flashlight battery, hydrogen and oxygen

would be formed, a high gas pressure would build up in the cell, and the cell could explode (a purely mechanical explosion). If there was a spark, the hydrogen and oxygen would combine explosively (a chemical explosion) and make things even worse. It is very dangerous.

In those few types of cells that can be recharged, the cell has been designed in such a way as to block the formation of hydrogen and oxygen and allow the appropriate charging reaction to go on. Note that in the charging of the lead storage battery a small amount of hydrogen and oxygen is formed, (the reaction has not been completely blocked) and constitutes an explosion hazard. It is essential to keep sparks and flames away from the car battery!

FINAL REMARKS:

Except when it involves the reaction of a dry gas (such as oxygen) with a dry piece of metal, the corrosion of metals takes place via a mechanism involving shortcircuited electrochemical cells. (See Fig. 10-5 in the text.) In moist air a layer of water forms on the metal. At one point on the metal, Fe^{+2} ions leave the metal and enter the water layer:

$$Fe \longrightarrow Fe^{2+} + 2e^{-}$$

The two liberated electrons leave this point and go through the metal to some other point, where they react with oxygen and water to form hydroxyl ions in the water layer:

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-}$$

The local concentrations of the ferrous ion (Fe^{2+}) and the hydroxyl ion (OH^{-}) produce a difference in voltage between the two points in the solution, this in turn produces a current flow carried by the ions in the solution between those two points.

Since the current flows more easily if there are dissolved salts in the water, the entire corrosion process will be more rapid in the presence of dissolved salts.

HANDS ON

1. *The next time you visit the drug store, take time to notice that the cells come in different physical sizes, but that the voltage is the same, 1.5 volts, regardless of size as long as the same chemical reaction is involved. The mercury cells used in some cameras and electronic equipment have a slightly lower voltage, 1.3 volts, because the chemical reaction producing the power is different.*

QUESTIONS

1. *Define oxidation and reduction in terms of electron changes.*
2. *Name a metal whose oxide coating protects the metal from further attack.*
3. *What important feature distinguishes the lead storage battery from the ordinary flashlight battery?*
4. *What invention made the heart pacemaker into a practical device?*
5. *What is the name of the process which uses electrical energy to convert low energy substances to high energy substances?*
6. *Name at least one metal that is produced industrially by electrolysis.*
7. *What is the source of the electrical energy that is produced by an electrochemical cell?*

UNIT 16

THE PROTON IN CHEMISTRY

BEFORE WATCHING

YOU ALREADY KNOW

Solutions of dissolved electrolytes conduct an electrical current.

READ

Chapter 9. Acids and Bases—Chemical Opposites (entire chapter)

OVERVIEW

The classical properties of acids and bases are demonstrated. For acids, sour taste, the ability to dissolve active metals such as magnesium with the liberation of hydrogen, the liberation of carbon dioxide from limestone, and the ability to change the color of vegetable dyes. For bases, bitter taste, lack of reaction with magnesium and limestone, and the ability to reverse the color changes produced by acids in vegetable dyes.

The distinction between strong and weak acids is explained. In aqueous solution every molecule of a strong acid reacts with water to produce a hydronium ion, while only a small fraction of the molecules of a weak acid react with water to produce hydronium ions. A similar definition distinguishes between strong and weak bases.

The industrial importance of acids and bases is illustrated by the use of sulfuric acid and phosphoric acids in the phosphate industry. The environmental impact of acid rain is also illustrated.

The Bronsted-Lowry definitions of acids and bases are described, and the role of water in acid-base chemistry is explained. The definition of pH is given, and the usefulness of this concept is explained. Some examples are given of the materials used to neutralize stomach acid.

WHAT TO LOOK FOR:

ACIDS AND BASES

a) acids
b) bases
c) strong and weak acids and bases

INDUSTRIAL FOOTAGE

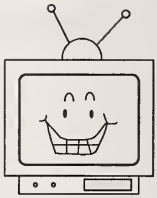
d) manufacture of fertilizers

ROLE OF THE PROTON

e) proton donors and proton acceptors
f) role of water
g) competition

pH

h) definition of pH
i) antacids



WATCH THE PROGRAM

AFTER WATCHING:

ACIDS AND BASES

a) Acids

In terms of its classical definition, an acid tasted sour, it changed the color of vegetable dyes (e.g., litmus), it dissolved metals such as iron and zinc with the liberation of hydrogen, and it reacted with limestone to liberate a gas, carbon dioxide.

These classical properties of acids are demonstrated by Don Showalter.

The sip of wine that has gone sour from standing open to air too long, the taste of lemon, both illustrate the sour taste of acids.

The change of blue litmus to red using lemon juice is typical of the kind of color changes that occur to vegetable dyes when acid is added to the dye.

Magnesium dissolves readily when an acid, such as hydrochloric acid, is added; the reaction is

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

The reaction of hydrochloric acid with limestone is typical:

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O + CO_2(g)$$

b) Bases

Classically, bases were defined as having a bitter taste, being able to undo the change in color of vegetable dyes produced by an acid, and being capable of reacting with acids to produce a neutral substance (a substance which is neither acidic nor basic) called a salt.

The bitter taste of a base can be experienced by tasting sodium bicarbonate, baking soda.

The Showalter demonstration shows the change from red to blue when the litmus paper is exposed to the base, ammonia.

There is no reaction of the ammonia with either magnesium or with limestone.

The reaction of an acid with a base is shown in three experiments. The vapors of HCl and ammonia from the bottle stoppers diffuse towards one another and react to form a smoke consisting of ammonium chloride.

$$HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$$

In the second reaction, a solution of nitric acid is added to a solution of sodium hydroxide (a base); they react to form water and a salt. But nothing is visible since all three substances are colorless.

$$HNO_3(aq) + NaOH(aq) \longrightarrow H_2O + NaNO_3(aq)$$

In the final example, acetic acid reacts with sodium bicarbonate to form sodium acetate, water, and carbon dioxide gas.

$$HOOCCH_3(aq) + NaHCO_3(s) \longrightarrow NaOOCCH_3(aq) + H_2O + CO_2(g)$$

c) Strong and weak acids and bases

We distinguish between strong acids such as nitric, sulfuric, and hydrochloric acid, and weak acids such as acetic acid (the principal constituent of vinegar) and citric acid (the acidic constituent in citrus juices). In water solution the distinction between these two classes of acids is based on the extent to which they react with water to produce a hydrated hydrogen ion (hydronium ion). For example, in water a strong acid such as hydrochloric acid reacts with the water, thus,

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

If essentially all the HCl undergoes this reaction, that is, if there is only a negligible amount of unreacted HCl remaining, then the acid is called a **strong** acid.

On the other hand, if only a small fraction of the acid undergoes this reaction and most of the acid remains unreacted, the acid is called a **weak** acid. Hydrocyanic acid, for example, undergoes the reaction,

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

but only to a very slight extent. In a solution containing 0.1 mol/L of HCN, only 7 molecules of HCN in every 100,000 have reacted in this way. In a 0.1 mol/L solution of acetic acid, only about 1300 molecules of acetic acid in 100,000 undergoes this reaction. There is an equilibrium established in solutions of weak acids, hence the arrow in the reaction is double-headed. The rate of the reverse reaction is equal to the rate of the forward reaction when there is only a small concentration of the hydrated protons, H_3O^+, present.

To compare the three acids, all in solutions having the same concentration of 0.1 mol/L, we tabulate the number of hydrogen ions produced per hundred thousand molecules of the acid.

Acid	Number of H_3O^+ ions/100,000 molecules of acid
HCN	7
Acetic	1300
HCl	100,000

Clearly, the strength of the acid can be judged by the number of hydrogen ions that are produced in this reaction. HCl is a strong acid; every molecule of HCl produces a hydrogen ion. Both HCN and acetic acid are weak acids, but HCN is weaker than acetic acid.

Measurements of the amount of hydrogen ion produced by a given amount of acid led to this classification of acids into strong and weak, as well as giving us a way to grade the weak ones.

In a similar way we can speak of a strong base, OH^- ion, that eagerly accepts a proton from the weakest of acids. In aqueous solution we can measure the strength of a base by the fraction of molecules that produce OH^- ions when dissolved in water. For example,

Base	Number of OH^- ions/100,000 molecules of base
$C_6H_5NH_2$	7
NH_3	1300
NaOH	100,000

Thus, it is clear that all of the NaOH produces OH^- in water, so NaOH is a strong base. Only seven molecules of aniline in every hundred thousand react with water to produce OH^-, so aniline is as weak a base as HCN is a weak acid.

INDUSTRIAL FOOTAGE

d) Manufacture of fertilizers

We manufacture more sulfuric acid, judged by mass, than any other industrial chemical. It is used as a source of hydrogen ion in many chemical syntheses, e.g., in making volatile acids such as HCl and HNO_3, in many organic syntheses, and in the manufacture of fertilizers.

About 65% of the sulfuric acid produced goes into the manufacture of fertilizers: ammonium sulfate, ammonium nitrate, and phosphate fertilizers of various kinds.

A typical phosphate rock has the composition, $Ca_5(PO_4)_3F$. This form of calcium phosphate is too insoluble to be used as a fertilizer to supply phosphorus to plants. When it is treated with sulfuric acid it forms calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, which is soluble enough to be a fertilizer.

The reaction is:

$$2Ca_5(PO_4)_3F(s) + 7H_2SO_4(l) + 3H_2O(l) \longrightarrow 3Ca(H_2PO_4)_2{\cdot}H_2O(s) + 2HF(g) + 7CaSO_4(s)$$

The solid mixture of calcium dihydrogen phosphate hydrate and calcium sulfate can be spread directly on the land as a source of phosphorus.

If more sulfuric acid is used, the phosphate can be converted entirely to phosphoric acid.

$$Ca_5(PO_4)_3F(s) + 5H_2SO_4(l) \longrightarrow 5CaSO_4(s) + 3H_3PO_4(l) + HF(g)$$

The liquid phosphoric acid can be removed from the solid calcium sulfate by filtration.

If the phosphate rock is treated with phosphoric acid, it is converted to "triple superphosphate" fertilizers.

$$Ca_5(PO_4)_3F(s) + 7H_3PO_4(l) \longrightarrow 5Ca(H_2PO_4)_2(s) + HF(g)$$

These fertilizers contain no calcium sulfate and hence are richer in phosphorus.

Sulfuric acid can be combined directly with ammonia to make ammonium sulfate, a nitrogen fertilizer. Other nitrogen fertilizers include ammonium nitrate and ammonium phosphate.

ROLE OF THE PROTON

e) proton donors and proton acceptors

In the late nineteenth century Svante Arrhenius, through an examination of the electrical conductivity of solutions of acids and bases, suggested the division into the two classes, strong and weak, that we use today. He also suggested that an acid was any compound that dissolved in water to yield hydrogen ions and a base was any compound that dissolved in water to yield hydroxide ions. The reaction between an acid and a base was considered to be the reaction of a hydrogen ion with an hydroxide ion to yield water.

$$H_3O^+ + OH^- \longrightarrow 2H_2O$$

Much later Bronsted and Lowry defined an acid as any compound that could donate a proton to a base, which in turn was any compound that could accept a proton from an acid. These are the definitions that we will use here. These definitions lead to an important insight into the role of water in acid-base equilibria.

f) the role of water

Consider what happens when HCl is dissolved in water:

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

We see that the HCl molecule donates a proton to the water molecule. Thus, HCl is an acid and the water is a base. If we examine the reverse reaction, we see that the hydronium ion, H_3O^+, donates a proton to the Cl^- ion. Thus, H_3O^+ is an acid and Cl^- is a base. Thus, in this simple little reaction there are two acids and two bases. Which is the stronger acid? HCl or H_3O^+? Since at equilibrium there is no HCl present, it must be that HCl is the stronger acid, because it was able to give away all its protons while H_3O^+ cannot give back any to reform HCl. By the same argument, H_2O is the stronger base, since it can accept the proton easily from HCl while Cl^- cannot accept any from the hydronium ion.

Consider the equilibrium

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

In this case, we have essentially all HCN molecules and very few CN^- ions. The HCN is the weaker acid since it can only give away a few of its protons, while the hydronium ion gives away almost all of its protons. Similarly, CN^- is a stronger base than water since it can accept a proton readily to form HCN while water can barely accept the proton from HCN.

Consider the reaction between water and ammonia, which is a base.

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

In this case, water donates a proton to the ammonia molecule, the acceptor. Thus, we see that water can act either as an acid or as a base, depending on the other reagent. Because of this ability to act in either way, water is called an **amphiprotic** substance.

In pure water, some hydronium and hydroxyl ions are produced by the ionization of the water molecule.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

At 25 °C the concentration of hydronium ions is 10^{-7} mol/L and is equal to the concentration of the OH^- ions. Since the concentrations of these two ions is equal in pure water, pure water is a neutral substance. The existence of these few ions confers a very tiny electrical conductivity on water. At room temperature only one in about 500 million molecules undergoes this reaction.

g) competition

The idea of competition is inherent in the Bronsted-Lowry definition of acids and bases. The behavior of a substance as an acid or a base is never exhibited by itself but only in connection with the acid-base properties of another substance.

For example, the dyes that change colors in the presence of an acid or base are themselves acids and bases. Let B^- be the blue form of litmus, and BH the red form; then when we add acid to the blue form we have the reaction:

$$\underset{\text{blue}}{H_3O^+ + B^-} \rightleftharpoons \underset{\text{red}}{HB + H_2O}$$

The reaction is written with a double-headed arrow since it is, in fact, an equilibrium. Addition of acid to the system pushes the reaction to the right side, and the red form dominates. On the other hand, if we add a base, hydroxyl ion, the hydronium ion on the left side of the reaction will be consumed and the equilibrium will shift to the left to produce more hydronium ion and, along with it, more of the blue form of the dye.

pH

h) definition of pH

The concentration of hydrogen ion in solution can vary over an enormous range: commonly, from about 1 mol/L to 10^{-14} mol/L. Some simple way to describe this variation was needed. Sorenson invented the pH function, which is defined by concentration of hydrogen ion = 10^{-pH} mol/L.

For illustration, consider the table:

pH	conc of hydrogen ion
0	10^{-0} mol/L = 1 mol/L
1	10^{-1} mol/L = 0.1 mol/L
.	.
.	.
.	.
7	10^{-7} mol/L = 0.0000001 mol/L
8	10^{-8} mol/L = 0.00000001 mol/L
.	.
.	.
.	.
14	10^{-14} mol/L = 0.00000000000001 mol/L

Since water is neutral, and the hydrogen ion concentration is 10^{-7} mol/L, the pH of water is 7. Solutions having concentrations of hydronium ion greater than 10^{-7} mol/L have values of pH less than 7. Solutions with values of pH greater than 7 are basic. A one mole per litre solution of a strong base such as NaOH has a pH = 14.

In water solutions the product of the concentration of the H_3O^+ ion and the concentration of the OH^- ion must always be 10^{-14}. Thus, in one mole per litre of OH^- the concentration of H_3O^+ must be 10^{-14}mol/L; hence the pH is 14. In pure water the concentrations of H_3O^+ and OH^- are both equal to 10^{-7} mol/L; and, again, the product is 10^{-14}.

l) antacids

An antacid is a substance that can be ingested without injury and that is mildly basic. The base in the antacid neutralizes the excess acid in the stomach. It should be borne in mind that the stomach juices are normally quite acidic since the digestive enzymes function best in acid solution. Pain is felt only if the amount of acid is excessive or if the stomach juices reflux into the esophagus. Some typical bases that are used are:

Baking soda; sodium bicarbonate; $HCO_3^- + H_3O^+ \longrightarrow 2H_2O + CO_2$

Milk of magnesia; $Mg(OH)_2$ $Mg(OH)_2 + 2H_3O^+ \longrightarrow 4H_2O + Mg^{2+}$

Limestone; calcium carbonate; $CaCO_3 + 2H_3O^+ \longrightarrow 3H_2O + Ca^{2+} + CO_2$

Aluminum hydroxide; $Al(OH)_3$; $Al(OH)_3 + 3H_3O^+ \longrightarrow 6H_2O + Al^{3+}$

These substances and others are used in various combinations in the various commercial formulations.

HANDS ON

1. *Note the change in color when lemon is added to a cup of tea. This color change is not as dramatic as that of the red cabbage but is another example of a natural plant dye whose color depends on the pH.*

2. *Put about a cup of water in a pan, add about a cup of shredded red cabbage and bring the mixture to a boil. Simmer for about 15 minutes. Drain the colored water into a clear glass and let it cool. Add a pinch of baking soda to a tablespoon of the liquid in a saucer and stir until dissolved. Note the color. The solution is now basic. Now add vinegar a few drops at a time until the color changes back to the original color, showing that it is now acid. Repeat the experiment using lemon juice instead of vinegar.*

QUESTIONS

1. *What is an acid?*

2. *What is the species that gives an aqueous solution of an acid the characteristic properties of an acid?*

3. *Consider the chemical reactions:*

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$
$$KOH + HCl \longrightarrow KCl + H_2O$$

Write one equation that describes the chemical action that occurs in all three equations.

4. *Which of the following gases can dissolve in rain droplets in the atmosphere to produce acid rain?*

   a) ozone *b) sulfur dioxide* *c) nitrogen* *d) oxygen*

5. *Which of the following situations is best described by the phrase, "has a hydrogen ion concentration of 10^{-7} mol/L"?*

   a) a solution with a pH of 7 *b) an aqueous acid solution*

   c) rain water *d) an aqueous basic solution*

6. *Which contains more acid, a green apple or a ripe apple? Why?*

7. *What is the pH of each of the following solutions:*

   a) 0.1 mol/L HCl *b) 0.00001 mol/L HCl*

   c) 1.0 mol/L NaOH *d) 0.0001 mol/L NaOH*

UNIT 17

THE PRECIOUS ENVELOPE

BEFORE WATCHING

YOU ALREADY KNOW

How to interpret chemical reactions.

How acids and bases behave.

READ

Chapter 18. Clean Air--Should it be taken for Granted? (entire chapter)

OVERVIEW

The composition of the normal atmosphere is described and a few of the most important pollutants are listed.

The protective function of the ozone layer is described and the observations that show the depletion of the layer, particularly in the Antarctic, are illustrated. The threat to the ozone layer is detailed and one mechanism by which chlorine atoms destroy ozone is presented.

Our model for the composition of the earth's primitive atmosphere and a general idea about the chemical evolution of life forms is outlined.

Two geologic cycles, the water cycle and the carbon dioxide-oxygen cycle, are used as examples of how a dynamic balance is maintained in the earth's envelope.

The "greenhouse" effect is described and some reasons for its significance are given.

WHAT TO LOOK FOR

ATMOSPHERIC COMPOSITION

a) major constituents plus pollutants

OZONE LAYER

b) protective nature of the ozone layer
c) the mechanism for ozone destruction
d) ozone at ground level

PRIMITIVE ATMOSPHERE

e) chemical evolution

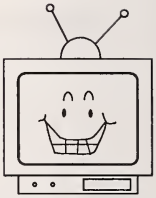
GEOLOGIC CYCLES

f) hydrologic cycle
g) carbon dioxide—oxygen

GREENHOUSE EFFECT

h) how it works

WATCH THE PROGRAM



AFTER WATCHING

ATMOSPHERIC COMPOSITION

a) major constituents plus pollutants

Dry air consists of three major constituents:

Substance	Formula	mol %
Nitrogen	N_2	78%
Oxygen	O_2	21%
Argon	Ar	1%

In addition to these gases there are constituents such as the noble gases, neon, helium, krypton, and xenon, that are present in very small amounts, 0.002%. Then there are gases such as water vapor, carbon dioxide, and hydrogen, whose proportions are variable depending on time and geographical location.

In ordinary air, as opposed to dry air, there is often a substantial amount of water vapor present. For example, on an 30 °C (86 °F) day with a relative humidity of 100% the composition of the air would be

Substance	mol %
Nitrogen	75
Oxygen	20
Water	4
Argon	1

On a 38 °C (100 °F) day with 100% humidity, the air would contain about 7% water vapor.

Other constituents are classified as pollutants. These would include particulate matter (dust), carbon monoxide, carbon dioxide if there is an excessive amount present, hydrocarbons (including unburned ones from automobiles and furnaces, as well as those exuded from trees), nitrogen oxides, and sulfur oxides. Ozone near ground level is regarded as a pollutant.

OZONE LAYER

b) the protective ozone layer

The radiation we receive from the sun extends from the infrared through the visible into the near ultraviolet. But it cuts off sharply a little below 300 nm. Only a tiny fraction of the radiation emitted by the sun with wavelengths below 300 nm reaches the earth. The reason for this is the presence of ozone in the stratosphere.

The fraction of the incident radiation from the sun that is transmitted through the atmosphere is called the transmittance; it is shown as a function of wavelength in the table below. The values in the table are based on the absorption by the ozone in the stratosphere.

Wavelength/nm	Transmittance
340	0.99
320	0.81
310	0.44
300	4.8×10^{-2}
290	2.5×10^{-4}
280	4.0×10^{-15}
260	1.0×10^{-39}
240	2.5×10^{-28}
220	1.0×10^{-6}

The first entry shows that the ozone layer transmits 99% of the radiation at 340 nm. As we move further into the ultraviolet, the amount transmitted decreases. At 300 nm, only 4.8% is transmitted. The ozone layer effectively cuts off any radiation below about 290 nm; for this reason stellar spectra cannot be observed at wavelengths shorter than 290 nm. Although the ozone is distributed throughout the atmosphere, its concentration is highest in the stratosphere. The total amount of ozone in the atmosphere is calculated to be the same as the amount that would be in a layer 3 mm thick at the earth's surface under a pressure of 1 atm at 0 °C; hence the expression, "ozone layer".

This ozone layer makes life on earth possible. If we were not protected from this short wavelength, high energy, ultraviolet radiation by this ozone layer, we would be killed within a short time by exposure to it. Even if only a part of the ozone is destroyed, there will be a significantly higher incidence of skin cancer. Today there is grave concern over the fact that the ozone layer is being slowly destroyed as a consequence of the presence of chlorine atoms in the upper atmosphere. The chlorine atoms are produced by the photodecomposition of chlorofluorocarbons (CFCs) in the upper atmosphere.

The production of CFCs is a billion dollar business. The major use of CFCs is as refrigerants; essentially all domestic refrigerators and air conditioners use CFC refrigerants. Beyond that, CFCs are used for solvents in cleaning microcircuit boards during their manufacture. Twenty years ago, CFC's were used extensively as propellant gases in spray cans of toiletries, foods, etc. These nonessential uses are now illegal in the USA. Today an intensive effort is underway to develope alternative compounds for use as refrigerants. Refrigeration is a necessity today if the food we grow is not to rot before it can be consumed. It is equally essential that the ozone layer be preserved so that we can live long enough to eat our next meal. Fortunately, some progress has been made in the search for substitute refrigerants.

c) the mechanism for ozone destruction

When CFCs are spilled or leak from refrigerators, the molecules escape as vapor into the atmosphere. Ultimately they diffuse to the stratosphere, where they interact with light from the sun to produce one or more chlorine atoms.

$$\text{CFC} + \text{light} \longrightarrow \text{Cl} + \text{other fragments}$$

The chlorine atom can then react with an ozone molecule:

$$\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2$$

The chlorine monoxide molecule can react with a free oxygen atom to produce diatomic oxygen and regenerate the chlorine atom:

$$\text{ClO} + \text{O} \longrightarrow \text{O}_2 + \text{Cl}$$

The chlorine atom is now free to repeat the sequence and destroy another ozone molecule in the process.

This sequence of reactions, in which an active species produces a result (in this case the destruction of an ozone molecule) and then is regenerated, is called a chain reaction. As a consequence of the chain reaction, one active species can cause the destruction of many (hundreds or thousands or millions) ozone molecules. Clearly, the more CFC moleculès that enter the atmosphere the greater the rate of destruction of the ozone molecules. The situation has prompted global concern and needs an international response. Our knowledge and understanding of this problem, while considerable, is still tentative in some of its aspects. Watch for the latest developments.

d) ozone at ground level

Ozone is produced in electrical storms and near electrical equipment when sparks jump across an air gap. It has a characteristic sharp, irritating odor. Ozone in the atmosphere near ground level is a pollutant. In the presence of nitrogen dioxide, ozone is produced photochemically and combines with hydrocarbon pollutants to

produce photochemical smog, an acrid, irritating material that can be hazardous to breathe.

PRIMITIVE ATMOSPHERE

e) chemical evolution

When the earth was first formed, we believe that the atmosphere consisted mainly of methane, CH_4, ammonia, NH_3, and water, H_2O. Lightning passing through this mixture ultimately produced organic molecules. We believe that these organic molecules included the amino acids and nucleic acids, the building blocks of the molecules that are necessary to living organisms. This primeval situation has been simulated in the apparatus shown in the program. Two flasks are connected so that the mixture of gaseous methane, ammonia, and water can circulate between them; the lower flask contains a liquid mixture of these three substances. For a long period a spark is passed through the gaseous mixture to simulate the lightning discharge in the atmosphere. Traces of organic materials, including amino acids and nucleic acids, have been identified in the lower flask.

The seas on the primitive earth became a primordial soup that contained the molecules necessary for the development of life. After millions of years, the first life forms emerged and, much later, organisms capable of photosynthesis developed. Ultimately all the diverse life forms came to be.

GEOLOGIC CYCLES

f) the hydrologic cycle

The hydrologic cycle is one of the simpler geologic cycles. In this cycle, sunlight falls on the surface of the sea and water is evaporated. Driven by winds which are also solar-powered, some of the moisture moves over land, and much is transported to high altitudes where the cooler temperature condenses it to cloud. Finally, it falls as rain or snow. The portion that falls on the land can nourish crops, produce power, and provide fresh water for drinking. Our very lives depend on the existence of this cycle of changes.

g) the carbon dioxide-oxygen cycle

Another cycle of changes provides us with life-giving oxygen to breathe. This cycle involves the photosynthesis of carbohydrates by plants. This reaction can be written in a general way as

$$nCO_2 + nH_2O + \text{light} \longrightarrow (CH_2O)_n + nO_2.$$

The formula, $(CH_2O)_n$, is a general formula for a carbohydrate. The photosynthesis reaction goes on in green plants through the mediation of the green pigment, chlorophyll. The demonstration by Don Showalter shows dramatically that the carbon dioxide is consumed by the plant. We rely on this reaction for our supply of oxygen. In turn, the respiration process in both plants and animals requires oxygen and produces carbon dioxide.

Before the industrial revolution, the main sources of carbon dioxide in the atmosphere were volcanic gases, the burning of forests, and domestic uses of coal and wood for fuels, as well as the amounts produced by respiration of plants and animals. The largest sink for carbon dioxide is in the oceans, in which it dissolves to form both carbonate and bicarbonate ions:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

In a slightly alkaline medium we have

$$H_2CO_3 + OH^- \longrightarrow H_2O + HCO_3^-$$

and to a lesser extent

$$HCO_3^- + OH^- \longrightarrow H_2O + CO_3^{2-}$$

The CO_2 in the ocean is consumed mainly in two ways: photosynthesis by microscopic plants, and combination with calcium and magnesium ions to form the carbonates. The principal constituent of clam and oyster shell is calcium carbonate, $CaCO_3$.

Since the industrial revolution, enormous increases in the use of fossil fuels, coal and oil, have occurred. Burning these fuels increases the amount of CO_2 in the atmosphere. The presence of large amounts of polyatomic gases in the atmosphere produces the so-called "greenhouse" effect.

GREENHOUSE EFFECT

h) how it works

Dry air has an extraordinary property; it is transparent to infrared radiation. Symmetrical diatomic molecules such as oxygen and nitrogen do not absorb in the infrared, nor do monoatomic molecules such as argon and the other noble gases. The infrared region of the spectrum is the region of heat waves. When you put your hand near a hot surface, the warmth that you feel is the infrared radiation that is given off by the hot surface and is absorbed by your hand.

To understand the greenhouse effect it is necessary to understand that every object emits radiation; the range of frequencies emitted depends on the temperature of the object. A hot object such as the sun, with a surface temperature of 6000 K, has a

maximum energy emitted at a wavelength of about 500 nm, which is in the green region of the spectrum. But enough light having frequencies on both sides of this maximum is also emitted that we perceive the sun as a source of white light (a mixture of all frequencies in the visible region). As the object cools the wavelength of the maximum emission moves toward the red region of the spectrum. The filament in the ordinary incandescent lamp is at about 3000 K and it too emits sufficiently over the entire visible spectrum so that the light appears white. Objects at about 1000 K appear to be "red hot" instead of "white hot". Objects at room temperature, 300 K, have a maximum in the emission curve near 10000 nm, which is in the near infrared.

Now consider what happens if the surface of the earth at 300 K is allowed to radiate through a dry atmosphere. The infrared radiation emitted passes through the atmosphere without being absorbed and travels on into outer space. Because energy is carried away into outer space by the radiation, the earth's surface cools noticeably. This effect is pronounced in desert regions (no water in the atmosphere) and in ancient times was used in the Near East to make ice. Water in shallow layers easily freezes in the desert at night.

Suppose that instead of being transparent to the infrared rays there is an absorber such as water in the atmosphere. In particular suppose there is **a lot** of water present; it's a cloudy night. Now the outgoing infrared radiation is absorbed by the clouds. The energy is not carried off into outer space but is held by the cloud layer; this cloud in turn radiates and returns some of the radiation back to the earth's surface. The earth's surface does not cool very much so we observe that on cloudy nights the temperature does not drop as much as on a clear night. (This assumes that a weather front does not move through.) In a greenhouse the glass is the infrared absorber. The greenhouse warms during the day because the visible light from the sun can pass through the glass and warm the objects inside, but at night the infrared emitted by those objects cannot escape, so the greenhouse stays warm.

Carbon dioxide is an infrared absorber. The great concern is that as more and more carbon dioxide is allowed to enter the atmosphere the earth's temperature will become warmer. This global warming can have all sorts of untoward consequences; melting of the polar icecaps, with consequent rise in sea level leading to the inundation of lowlands. Gross changes in climate patterns might be possible; e.g., deserts and arable land changing places.

Other gases are also infrared absorbers: the CFCs are examples of polyatomic gases that can contribute to the greenhouse effect.

HANDS ON

1. *Listen for references to the greenhouse effect in weather broadcasts. For example, "The cloud cover will keep us warm tonight." or "The air is very clear tonight, frost may appear in exposed areas."*

2. *On a very clear night put two shallow pans of water outside, resting on a piece of wood or other heat insulating material. One should be open to the sky, the other under the roof on a porch; measure the temperature of each sample of water when they are first put out and again early in the morning before the sun hits them.*

3. *Hold your hand about a foot to one side of (not above) a burner on the stove or another hot surface. With the other hand hold a sheet of window glass near your hand between the burner and your hand. Notice the difference in sensation.*
   CAUTION: *Don't hold the glass too near the burner. It will shatter from the heat.*

QUESTIONS

1. *What are the four main constituents of air?*

2. *In what region of the spectrum does ozone absorb strongly?*

3. *The chemical steps in the decomposition of ozone through the mediation of chlorine atoms make up a chain mechanism. What is it about this mechanism that makes even very small concentrations of chlorine atoms very hazardous to the ozone layer?*

4. *Why is the ozone in the stratosphere referred to as "the ozone layer"?*

5. *Suppose that all photosynthesis stopped suddenly. What would happen to the amount of oxygen in the atmosphere? What would happen to the amount of carbon dioxide?*

6. *Name two gases which, if released into the atmosphere, will contribute to the greenhouse effect.*

7. *a) What processes remove oxygen from the atmosphere?*
   b) What processes add oxygen to the atmosphere?
   c) What processes remove carbon dioxide from the atmosphere?
   d) What processes add carbon dioxide to the atmosphere?

UNIT 18

THE CHEMISTRY OF EARTH

BEFORE WATCHING

YOU ALREADY KNOW

Acids and bases.

Covalent bonds.

Architecture of molecules.

READ

Chapter 11: "Silicon Materials-Old and New"; "Glass"; "Ceramics"; "Portland Cement and Concrete"; ""Pure" Silicon and "The Chip""

OVERVIEW

Some typical examples are cited of the nonuniform geographical distribution of the world's mineral resources.

The main processes by which mineral deposits are formed and segregated from other materials are reviewed in general terms.

The program then focusses on two ordinary materials, limestone and sand, to show how important these commonplace substances are to the beauty of the natural world, to our civilization, to art, and to technology. These are exemplified in the formation of limestone caves, the use of limestone in buildings and in statuary, and, finally, in the use of silicon in the computer chip.

WHAT TO LOOK FOR

DISTRIBUTION OF ORE DEPOSITS

a) examples: Cr, Pt, Rh, Co, Sn

PROCESSES FOR FORMING MINERALS

b) magmatic
c) hydrothermal
d) sedimentation

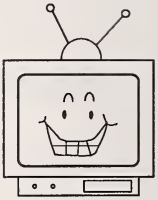
LIMESTONE

e) uses
f) demonstration of chemical composition and properties
g) caves

SILICATES

h) structural features of silicate minerals
i) purification of elemental silicon
j) products made from silicon

WATCH THE PROGRAM



AFTER WATCHING

DISTRIBUTION OF ORE DEPOSITS

a) examples: Cr, Pt, Rh, Co, Sn

One of the intriguing things about the earth is that there are places on it in which certain elements are concentrated. We find diamonds in South Africa and Australia, chromium and platinum in South Africa and the Soviet Union, molybdenum and tungsten in Colorado, gold and silver in the far western parts of the U. S., and so on. The fact that most elements are concentrated in deposits that can be exploited as ores is an enormous advantage to us. Consider the opposite case; suppose that the elements on the earth were all uniformly mixed. What a difference. For example, metals such as copper, silver, and gold would be too difficult to recover because there is so little of them. We could still extract iron, aluminum, and silicon; possibly, we would obtain magnesium and titanium. None of the other common metals would be extractable. Limestone and the silicates are common enough, so we could still make cement and build buildings. But much of what we do would not be possible.

In "Fiddler on the Roof", Tevia, the poor man, asks a profound question. "Would it upset some great, divine, and universal plan if I were a wealthy man?" We don't know the answer to Tevia's question, and we don't know the answer to the corresponding geological and geographic questions about why some nations are situated so that they have great mineral resources while others do not. But we can discuss the general processes that are involved in the transport of materials and the formation of mineral deposits.

PROCESSES FOR FORMING MINERALS

b) magmatic processes

The molten material in the interior of the earth is called **magma**. In this molten material, we can expect that any free metals such as iron and nickel being much denser than the oxides of the various elements, will sink to the center. This applies also to the very heavy metallic elements; although their abundance is low, they will tend to concentrate in the core. Since many of these heavy elements are naturally radioactive, we can reasonably expect that the center of the earth is radioactive. As the magma cools slowly, different materials crystallize at different stages of the

cooling. In general, the substances having the highest melting points and present in the largest proportion crystallize first. So we expect that quartz (SiO_2) and the silicates will crystallize first. These silicates are much less dense than the iron core and thus form a crust that floats on the core. As the more common elements are removed from the melt the rarer elements are concentrated in the melt. In the late stages of the solidification, minerals containing the rarer elements crystallize out. These may be found in seams (veins) between large chunks of material that have solidified earlier.

c) hydrothermal processes

As water condensed on the cooling earth it filled all the cracks and fissures that were available to it. Since the interior of the earth is hot the water became hot. This hot water dissolved soluble compounds as well as low melting substances like sulfur. This molten sulfur can react with hot metal surfaces to form sulfide minerals. Silica is soluble in hot alkaline water, and on cooling this solution can produce beautiful quartz crystals. The mineral deposits observed around the recently discovered black smokers on the ocean bottom provide another example of transport of materials by hydrothermal action.

Remnants of this hydrothermal action near the surface of the earth are exhibited by the geysers in the Yellowstone Park area and the geothermal fields in California.

d) sedimentation

The tiny grains of sand and other rock that are carried by rushing streams of water ultimately are deposited where the stream flows slowly. The buildup of these sediments over geologic ages ultimately compresses them into hard stony materials. Sandstone, marble, and limestone are typical of sedimentary rocks.

LIMESTONE

e) uses

Sedimentary rocks tend to be softer than igneous rocks such as granite, and so have been used throughout the ages for building stones. The pyramids at Ghiza and the sphinx, for example, are made of limestone. Many of the classic buildings in the Western Hemisphere are built of limestone or marble. Much artistic work on buildings and outdoor sculpture is made of limestone. Unfortunately, acid rain is taking its toll on these structures. Marble and limestone are soluble in acid.

f) demonstration of chemical composition and properties

Both limestone and marble consist of calcium carbonate, $CaCO_3$. Dolomite or dolomitic limestone is a mixture of calcium carbonate and magnesium carbonate. The great variety of color in marble is simply due to relatively small amounts of colored minerals of various kinds that are mixed with the calcium carbonate.

One of the most important chemical properties of limestone is that it dissolves in acid, even in solutions that are only slightly acidic. The reaction with hydrochloric acid is

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The calcium chloride is very soluble in water.

Acid rain often contains sulfuric acid. The reaction with sulfuric acid is

$$CaCO_3(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

In this case solid calcium sulfate is formed. But this solid is usually not strongly attached to the surface and is easily washed away by the rain or worn away by grit borne by the wind.

In a second demonstration Don Showalter prepares limewater and then precipitates calcium carbonate by adding carbon dioxide. Lime water is prepared by adding hydrated lime to distilled water and filtering off the undissolved solid. The lime water is a solution of $Ca(OH)_2$ in water.

When carbon dioxide is bubbled through lime water a white precipitate of calcium carbonate is formed. This is the classic chemical test for CO_2.

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

At this point we have a suspension of solid calcium carbonate in water. If we continue to bubble CO_2 through this suspension, the solid dissolves as the soluble calcium bicarbonate, $Ca(HCO_3)_2$, is formed. Thus,

$$CaCO_3(s) + H_2O(l) + CO_2(g) \longrightarrow Ca(HCO_3)_2(aq)$$

It is this last reaction that is involved in the formation of the stalactites and stalagmites in limestone caves.

g) caves

The last reaction occurs when water flows through underground passages and dissolves some carbon dioxide. This solution flows over some limestone and dissolves it, forming calcium bicarbonate, $Ca(HCO_3)_2$. This solution ultimately oozes out of a fissure in the rock and as the drop hangs in the open cave the reverse reaction occurs. CO_2 is released, and a tiny residue of insoluble calcium carbonate is left on the ceiling. Over thousands of years by this method a stalactite (from a Greek word meaning 'oozing out in drops') forms. If the drop falls first and then releases the CO_2, a tiny residue of calcium carbonate is left on the floor. After thousands of years a stalagmite (from Greek, 'a dropping') grows up from the floor. These marvelous and beautiful formations are possible simply because this chemical reaction can reverse itself depending on the temperature and the pressure of CO_2.

SILICATES

h) structural features of silicate minerals

Both carbon and silicon are members of the fourth family in the periodic table, so we might expect that their chemical properties would be quite similar. In fact, carbon and silicon are quite different chemically. In the case of carbon chemistry we find thousands of different kinds of carbon compounds, most of them containing some hydrogen, that are quite stable in the presence of oxygen and water. The activation energy for the reaction between oxygen and a hydrocarbon such as methane, CH_4, is quite high. As a result, the rate of oxidation is immeasurably slow in the absence of an initiating event. In contrast, the reaction between oxygen and compounds of silicon that contain hydrogen usually have very low activation energies. Thus, the compound silane, SiH_4, bursts into flame on contact with either oxygen or water vapor and burns to SiO_2. Among the elements, only fluorine forms a stronger bond with silicon than does oxygen. The single bond strengths of carbon to carbon, carbon to oxygen, carbon to hydrogen, and carbon to nitrogen are not greatly different. The practical result is that carbon chemistry is quite diverse, while silicon chemistry is exclusively the chemistry of silicon-oxygen compounds, that is, the chemistry of silicates.

The basic structural unit of the silicate minerals is the SiO_4 tetrahedron, with the silicon atom at the center and the four oxygen atoms at the corners of the tetrahedron. More complex silicates are formed when some of the oxygen atoms are shared between two tetrahedra. The program shows a simple example of chain formation in which every silicon-oxygen tetrahedron shares oxygen atoms with two other tetrahedra. There are many ways to form chains in addition to the one shown in the program. The fibrous silicates (asbestos is an example) have structures based on a chain of silicon-oxygen tetrahedra. If three oxygen atoms in each tetrahedron are shared with three other tetrahedra, a sheet structure results. Minerals such as mica and talc have structures based on silicon-oxygen tetrahedra connected in sheets. If four oxygens are shared with other tetrahedra we get the so-called "framework" silicates.

In all of these silicate structures, the silicon-oxygen units are bonded covalently, but there is a net negative charge on the unit so that, to build a neutral crystal, it is necessary to have positive ions present to hold the negative chains or sheets together. In that sense the silicates are ionic crystals.

i) purification of elemental silicon

Elemental silicon can be prepared by heating silica, SiO_2, with carbon and chlorine. This forms silicon tetrachloride:

$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

The $SiCl_4$ is then reacted with metallic sodium to produce the elemental silicon:

$$SiCl_4 + 4Na \longrightarrow Si + 4NaCl$$

The elemental silicon must be carefully purified before it can be used in semiconducting devices such as transistors and computer chips.

It was pointed out above that, when a liquid mixture is cooled, ordinarily the substance present in greatest proportion is the first thing to crystallize out of the melt. Furthermore, it is often the case that as the solid forms it excludes foreign atoms and does not incorporate them in the crystal. This is the reason for using recrystallization as a method of purifying materials. This property is used to produce silicon of incredibly high purity (less than 1 atom of impurity per billion atoms of silicon) by the method of zone refining.

Imagine a tube containing solid silicon being lowered slowly through a thin ring-shaped furnace. When the bottom of the tube reaches the level of the ring, the silicon melts. As the tube moves downward and the molten silicon drops below the level of the hot ring, pure silicon solidifies and leaves the foreign atoms in the melt. At this point the tube has pure solid silicon near the bottom, impure solid silicon near the top and a thin zone of molten silicon between them. As the silicon moves downward the molten zone moves through the impure silicon, collecting the foreign atoms as it moves. When the zone reaches the top, most of the foreign atoms have collected in the molten zone. The process is repeated several times. Each time the silicon bar that remains has a higher purity.

j) products made from silicon

Silicon is in a class of materials called semiconductors. This simply means that the electrical conductivity of silicon is not as large as that of metals and is not as low as that of insulators. The first measurements of the conductivity of silicon, made before the material was highly purified, differed greatly from sample to sample because of the **accidental** impurities in each sample. The measurements did not begin to make sense until highly purified silicon was available. It was found that the conductivity of the pure material was much lower than that of the impure material but that the conductivity could be increased and varied in a controlled way by the addition of minuscule amounts of substances from the neighboring groups in the periodic table; boron and phosphorus are often used.

By controlling the conductivity by "doping" the silicon with these tiny amounts of other elements one can produce composite devices having extraordinary capabilities. The first of these devices was the transistor, invented by J. Bardeen and W. H. Brattain in 1948. The transistor performs the same functions as the vacuum tube amplifier and the vacuum tube diode. The transistor has essentially replaced these vacuum tubes. The transistor, being several factors

of ten smaller than the vacuum tube that it replaced, challenged us to miniaturize equipment of all kinds. This activity, together with an explosion of invention that produced many kinds of semiconductor electronic devices, culminated in the invention of the computer chip, the pinnacle of achievement in semiconductor technology.

HANDS ON

1. *Put a tablespoon of vinegar in a glass of water and add a tablespoon of baking soda. Drop three moth balls into the glass. Observe the tiny bubbles of carbon dioxide that form. Observe where they form.*

QUESTIONS

1. *Gold is a very dense element, about twice as dense as iron. Would gold be expected to be more abundant in the earth's crust or in the core?*

2. *The density of silicate rocks varies between 2 and 3 g/mL. The density of iron is about 9 g/mL. Are these numbers consonant with the structure of the earth?*

3. *Write a chemical equation that describes the solubility of limestone in acid solution.*

4. *Write an equation that describes the solubility of limestone in carbonic acid (water saturated with CO_2).*

5. *Describe the processes involved in the formation of limestone caves.*

6. *What chemical processes are used to obtain silicon from sand, SiO_2?*

UNIT 19

METALS

BEFORE WATCHING

YOU ALREADY KNOW

Oxidation and reduction.

Electrolysis.

READ

Chapter 11: "Metals and their Reduction"; "Iron and Steel"; "Aluminum"

OVERVIEW

The broad variety of uses of metals is illustrated and their important physical properties are mentioned. The difference between active metals such as aluminum and a less active metal such as iron is dramatically demonstrated by the thermite reaction.

The atomic structure of metal crystals is shown by building layers of plastic balls. The structures in which the balls are most closely packed are the structures commonly found in metal crystals.

The reduction of iron oxide by hydrogen in the laboratory is demonstrated, as is the inability of hydrogen to reduce aluminum oxide. We move from the laboratory to the industrial production of iron in the blast furnace and then to the high temperature electrolysis of aluminum oxide to produce metallic aluminum.

Interviews with metallurgists whose efforts are devoted to the production of special alloys conclude the program.

WHAT TO LOOK FOR

PHYSICAL PROPERTIES

a. the metallic properties:

reflectivity or lustre
electrical conductivity
thermal conductivity
ductility
malleability
density, hardness, mechanical strength, resistance to chemical attack

ATOMIC STRUCTURE OF METALS

b. close-packing of spheres

CHEMICAL PROPERTIES

c. demonstrations

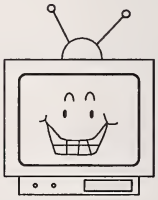
EXTRACTIONS

d. extraction of iron from its ores
e. extraction of aluminum from its ore

ALLOYS

f. from aluminum to zinc

WATCH THE PROGRAM



AFTER WATCHING

PHYSICAL PROPERTIES

a. The metallic properties

The program concentrates mainly on the physical properties of metals. The physical properties are:

Reflectivity or lustre: When this property of being able to take on a high polish is combined with resistance to tarnishing, the metal is useful for making decorative articles such as jewelry. Gold and platinum are particularly suited for this use, since they do not tarnish in air. Silver, brass, and copper tarnish slowly and so must be polished from time to time to remove the tarnish and maintain their brilliance.

Electrical conductivity: Metals, especially pure metals, are good conductors of electrical current. The principal use of pure copper is in electrical wiring and electrical machinery. Gold and silver and even platinum are used for electrical contacts on a smaller scale in specialty electronic applications where resistance to corrosion is of primary concern.

Thermal conductivity: Metals generally are very good conductors of heat. This makes them useful in heat exchange devices industrially, in the home furnace, and in the commonplace automobile radiator. By way of exception to this, some stainless steels are relatively poor heat conductors; for example, there is a stainless steel vacuum bottle on the market.

Ductility: Ductility is the property of being capable of being drawn into wires. This property is needed in addition to electrical conductivity to enable us to produce copper wire that will conduct a current.

Malleability: Malleability is the property of being capable of being hammered into thin sheets. This property is especially pronounced in gold; the gold leaf used in decorating articles has been hammered so thin that one can see through it.

Malleability and ductility contribute to the **plasticity** of the metal, that is, the ability of the metal to be deformed and shaped. The blacksmith who is shown forging a knife blade is taking advantage of the plasticity of the hot steel. So does a modern rolling mill that takes a huge bar of white hot steel and, by passing it through rollers, forms it into an I-beam to be used as part of the structural framework of a modern building.

Density, hardness, mechanical strength, and resistance to chemical attack are other properties that are important to the uses of metals.

ATOMIC STRUCTURE OF METALS

b. Close-packing of spheres

Almost all metals have one of the two close-packed structures demonstrated by the spheres in the graphic and in Don Showalter's construction with the plastic balls. These structures are called "close-packed" because, using these arrangements, we can pack the most spheres in a given volume. As a consequence of the close-packed structure, the electrons in the metal are free to wander throughout the entire crystal. In a general way, we can say that all the properties of metals flow from this structure.

Specifically, both the electrical and the thermal conductivity of metals are immediate consequences of the ability of the electrons to move freely through the metal. As the electrons move in an electrical field they carry electrical charge and thus an electical current. If there is a temperature difference between the sides of the metal, the electrons moving from the hot side of the metal carry more energy than those that move from the cold side. The net result is a transfer of a net amount of energy as heat from the hot to the cold side.

Lustre and reflectivity are also direct consequences of the presence of free electrons in the metal, but for reasons too intricate to be dealt with here.

Unfortunately, one cannot make an easy explanation for the mechanical properties such as ductility and malleability. These depend in a complex way not only on the atomic structure of the metal but also on the presence or absence of defects in the atomic arrangement, called "dislocations". In addition, mechanical properties may depend on the sizes of the microscopic grains in the metal, as well as kinds of foreign atoms that might be present in the grain boundaries.

For example, ductility and malleability depend on the ability of layers of atoms in the metal crystal to slip past each other. This cannot happen unless the electrons are free to move throughout the crystal and are not tied up in bonds between particular atoms which would hold the layers in a fixed position relative to one another. In a sense, the electrons act as a lubricating layer between the layers of atoms; but this is not enough. Unless there are defects in the atomic arrangement, slip will not occur. If special care is taken to grow pure metal crystals without these defects, slip occurs only with great difficulty, and the crystal can be subjected to enormous pulling stress before it yields.

CHEMICAL PROPERTIES

c. Demonstrations

The first demonstration in the program provides striking illustrations of the difference in affinity of metals for oxygen.

Platinum does not combine directly with oxygen under any circumstances. Heating the metal, as in the demonstration, only results in the metal glowing. The finish of the metal is as brilliant after heating as before. Platinum oxides do exist, but

they must be made by indirect methods.

The thermite reaction illustrates one of the most spectacular examples of a difference in the affinity of two metals for oxygen. Aluminum is an extremely active metal, much more so than iron. As a consequence it simply replaces iron in the compound, ferric oxide.

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$$

The half-reactions are:

$$Al \longrightarrow Al^{3+} + 3e^-$$
$$Fe^{3+} + 3e^- \longrightarrow Fe$$

So much heat is liberated in this reaction that the iron is produced in the molten state, and fragments of white-hot oxide and molten iron are strewn about the area.

The same difference in activity is illustrated in a different way by the second demonstration. Here, hydrogen is passed over small heated samples of ferric oxide and aluminum oxide. The hydrogen easily reduces the ferric oxide to metallic iron and water.

$$3H_2 + Fe_2O_3 \longrightarrow 3H_2O + 2Fe$$

The half-reactions are

$$H_2 \longrightarrow 2H^+ + 2e^-$$
$$Fe^{3+} + 3e^- \longrightarrow Fe$$

In contrast, hydrogen is unable to liberate the more active aluminum from its oxide.

EXTRACTIONS

d. Extraction of iron from its ores

The difference in reactivity of the two metals is reflected in the industrial preparation of iron and aluminum. Ferric oxide is reduced to metallic iron by

heating with carbon in a blast furnace. A charge of limestone, coke, and iron ore is added through the top of the furnace. A blast of hot air is forced into the furnace near the bottom. Some of the carbon burns to carbon monoxide.

$$2C + O_2 \longrightarrow CO$$

This reaction serves to heat the charge even more, and provides carbon monoxide for the reduction of the ferric oxide.

$$3CO + Fe_2O_3 \longrightarrow 3CO_2 + 2Fe$$

The limestone is decomposed to lime and carbon dioxide in the furnace:

$$CaCO_3 \longrightarrow CaO + CO_2$$

limestone lime

The lime combines with any silica that may be present to form calcium silicate,

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

lime silica calcium silicate

which floats on top of the molten iron and can be drawn off as a slag.

Some other common metals that are obtained by the reduction of the metal oxide by either carbon or carbon monoxide are: copper, nickel, zinc, tin, and lead.

e. Extraction of aluminum from its ore

The oxide of aluminum, Al_2O_3, is so stable that it is not possible to reduce it to aluminum using common reducing agents such as hydrogen, carbon, or carbon monoxide. The first samples of aluminum were obtained in the laboratory by using elemental sodium or potassium to reduce molten aluminum chloride. The reduction of aluminum oxide can be done by electrolysis, however. The process, devised in 1886 by Charles Martin Hall, consists of passing a current between carbon electrodes immersed in a solution made by dissolving aluminum oxide, Al_2O_3, in a molten mixture of cryolite, Na_3AlF_6, and calcium fluoride, CaF_2. The operating temperature is about 900 °C. This molten mixture contains aluminum ions and oxide ions, which are discharged at the electrodes when a current is passed through the mixture.

At the cathode: $Al^{3+} + 3e^- \longrightarrow Al$

Since the temperature is above the melting point of aluminum, 660 °C, the metal is formed in the molten state.

At the anode: $C + O^{2-} \longrightarrow CO + 2e^-$

$CO + O^{2-} \longrightarrow CO_2 + 2e^-$

Carbon monoxide and carbon dioxide are formed in about equal amounts at the anode, which is consumed in the process and must be regularly replaced.

Some other metals prepared by the electrolysis of their molten compounds are: alkali metals (Li, Na, K, Rb, Cs) and alkaline earth metals (Mg, Ca, Sr, Ba).

ALLOYS

f. From aluminum to zinc

When a metal is combined with other metals the result is called an **alloy**. The composition of alloys can vary over wide limits; for example, brass, an alloy of copper and zinc, can vary from being nearly pure copper to being nearly pure zinc. The properties of the brass depend very much on the relative amounts of copper and zinc present in the alloy. Nonmetallic elements such as hydrogen, boron, carbon, nitrogen, and even occasionally sulfur are also used as alloying elements.

The important point about alloys is that their properties can be drastically different from those of the pure elements that make them up. For example, pure iron is very soft and not very strong. When alloyed with carbon, it produces a series of alloys called carbon steels; the mild steels contain up to 0.2% carbon and are used in situations where strength is not a consideration. The medium steels, containing 0.2 to 0.6% carbon, are used for structural steels. The high carbon steels, containing 0.9% to 1.5% carbon, are very hard and are used for making tools. Note that very small changes in the percent of carbon makes drastic changes in the properties of the steel.

In the **carbon steels** the carbon atoms are very small compared to the iron atoms and so are able to occupy the interstices between the iron atoms in the metal; they are interstitial alloys. The presence of a foreign atom in these positions tends to reduce ductility and malleability. The alloy becomes harder, stronger, and may even become brittle. The atoms of hydrogen, nitrogen, and boron are also small enough so that they can form interstitial alloys with iron.

Another important type of alloy is the **substitutional alloy.** The low zinc brasses are an example. If we make a brass consisting of ten atom percent of zinc (that is, ten zinc atoms for every ninety copper atoms), then the atomic structure of the alloy is the same as that of pure copper, except that, on the average, every tenth atom of copper has been replaced by a zinc atom. The zinc atom simply substitutes for the copper atom in the metal lattice. The distances between the atoms increase slightly to accommodate the larger zinc atom. This replacement is random, so that

occasionally we will find zinc atoms next to one another. The properties of this alloy are, of course, quite different from those of pure copper.

In more complicated cases, actual compounds of a sort can be formed between the metal atoms. And, of course, many alloys contain several metals rather than just two.

One of the first alloys commonly used by mankind was **bronze**, *an alloy of copper and tin. Both of these metals can be won from their ores at relatively low temperatures, even the temperature of a campfire. One of the ages in the development of civilization, the Bronze Age, takes its name from this alloy. Before the advent of iron, bronze was commonly used for tools, armor, weapons, and sculpture.*

Today, we use thousands of alloys of all kinds, from the simple carbon steels that have been used for centuries to the exotic "super alloys" that are only a few years old. Today, we design alloys for very specialized purposes. The so-called "super alloys" are designed to withstand very high temperatures and stresses, as might be met in rocket engines, for example. The stainless steels were designed to resist corrosion. They contain large amounts of chromium and nickel; for example, a common stainless steel is called 18-8, because it contains 18% chromium and 8% nickel. Alloys of aluminum are used as structural elements in aircraft because of their light weight. Currently there is great interest in alloys with special magnetic properties. The list goes on and on.

Note that the superconducting material described by Roald Hoffmann is not a **metal** alloy. It is a solid composition of metal oxides.

HANDS ON:

1. *Obtain a piece of copper wire and a nail with approximately the same thickness. Try to bend each of them.*

   Note the difference.

2. *If you have a piece of steel that can be used as an anvil (the head of a sledge hammer, for example) put the nail on the anvil and try to flatten the nail along its length by hammering it. Do the same for the piece of copper wire.*

Note the difference.

3. *Observe the metal items that you come in contact with every day at home and in the work place.*

   What properties of the metal are necessary for this particular application?

   In which cases could the metal be replaced by plastic?

   Note the colors of the various metal items.

4. *Can you distinguish, just by eye, between a gold or gold-plated article and a brass or brass-plated one?*

5. *The sheet metal that is used to make the ductwork of a heating system is usually galvanized iron; that is, the iron sheet has been dipped in molten zinc.*

   Can you suggest a reason for this?

QUESTIONS

1. *Name three physical properties of metals.*

2. *Name two distinctive properties of metals that are a consequence of the delocalization of the electrons in the metal.*

3. *What does the thermite reaction tell us about the relative ease with which iron and aluminum lose electrons?*

4. *Name two materials that act as reducing agents in the production of iron in the blast furnace.*

5. *Describe the locations of the carbon atoms in a low-carbon steel.*

6. *Describe the arrangement of the atoms in a typical metallic structure.*

UNIT 20

ON THE SURFACE

BEFORE WATCHING

YOU ALREADY KNOW

Polarity.

Catalysts.

READ

Chapter 22: "Cleansing Agents"; "Soap"; "Synthetic Detergents"

OVERVIEW

This program presents a variety of phenomena that occur as a consequence of the special properties of surfaces. Surfaces behave the way that they do because of uncompensated forces acting on the atoms and/or molecules at the surface. The greater these forces, the more pronounced the behavior. For example, a molecule in the body of a liquid is pulled equally in all directions by the molecules around it. A molecule on the surface of a liquid is pulled downward by the molecules below it, but there are no molecules above it to balance that force. This imbalance gives rise to a surface tension; the liquid acts as if there were a contractile skin pulling the liquid together.

On surfaces of metals, ionic crystals, and covalent crystals there are unsatisfied bonding forces that act on atoms and molecules that come near the crystal. At the surface of a catalyst these unsatisfied forces may cause an approaching molecule to break up. The resulting fragments may be able to form bonds with the atoms on the surface. This is the mode of action of many catalysts. Unsatisfied bonding forces can also provide a way for adhesives to attach to other materials.

WHAT TO LOOK FOR

EXAMPLES OF SURFACE ACTION

a) computer chips, lubricants, detergents, adhesives, catalysts
b) the floating paper clip

FORCES AT THE SURFACE

c) graphic of forces
d) graphic of surfactant molecules

SURFACTANTS

e) uses of surfactants

ADHESIVES

f) a sticky problem

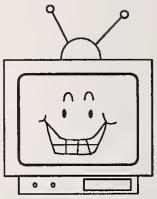
CATALYSTS

g) graphic of diatomic molecules on catalyst surface
h) Madey interview; modelling and measurements
i) acrylonitrile

SURFACE AREA

j) shapes of catalyst particles
k) surface area demonstration
l) zeolites

WATCH THE PROGRAM



AFTER WATCHING

EXAMPLES OF SURFACE ACTION

a) computer chips, lubricants, detergents, adhesives, catalysts

The construction and/or use of all the materials listed in the section head depends crucially on the properties of the surface between two distinct pieces of matter.

In the construction of the multilayer material that makes up the devices on a computer chip, the adhesion of one layer to the next requires that there be no intervening foreign atoms to prevent the two layers from sticking to one another.

The lubrication of a bearing in a machine requires properties opposite to the computer chip. The lubricating oil is inserted between two pieces of metal to prevent them from sticking to each other. If two clean metal surfaces are pressed together, they will stick together; if there is a layer of oil between them, they will not stick. The oil molecules between the two pieces of metal do not allow the metal atoms in one piece to get close enough to the metal atoms in the other piece to form a bond.

Detergent action depends on molecules, called surfactants, that have two parts. One part of the molecule "feels at home" in a nonpolar or oily liquid, while the other part of the molecule "feels at home" in a polar liquid such as water. Because of this two-part structure, they concentrate at the interface between two dissimilar liquids.

Adhesives, from various types of glues to the coatings used on tapes, pose special problems for the chemist, as we shall see below.

In heterogeneous catalysis, the chemical reaction takes place on the surface of the solid catalyst. Heterogeneous catalysts depend for their action on the special structure of the surface layer of the solid. In an earlier program, a rhodium catalyst was dissolved in a liquid; that was an example of a homogeneous catalyst, which simply is one of the reactants in a solution--no surface is involved.

b) the floating paper clip.

The molecules at the liquid surface are subjected to a force that tends to pull them into the body of the liquid. The attraction of the molecules in the center of the liquid pull them toward the center, but there is no force of attraction pulling them upward. This means that the liquid surface resists being increased in area. The floating paper clip provides an example of how the surface of a liquid can support a weight (the

paper clip). The experiment depends on the presence of a very thin layer of oil on the paper clip; the oil comes from the machinery that produces the paper clip or from handling it with our oily fingers. Now, when an oily paper clip is lowered gently onto the surface of the water, the surface water molecules see the oil molecules on the surface of the clip. The water molecules in the surface do not want to move over to make room for the oil molecules, since doing so would involve breaking strong water-to-water bonds and forming weak water-to-oil bonds. So, the clip is repelled by the surface and if it is light enough the clip will float. The addition of detergent to the water lowers the forces acting between the molecules of water in the surface and it removes the oily layer from the clip. Now the water wets the clip, and the clip sinks. Similarly, a detergent solution wets the waxed paper and the liquid no longer collects in droplets on the paper.

FORCES AT THE SURFACE

c) graphic of forces

The cartoon shows the forces acting at the surface of a liquid. The net force pulling the surface molecules towards the interior of the liquid is shown.

d) graphic of surfactant molecules

In this cartoon the water molecules are shown using the space-filling models, while the surfactant molecules are shown in a schematic way. In the surfactant molecule, the polar head, the large green sphere, is attached to a zigzag line. The zigzag line represents the nonpolar tail of the molecule, usually a long hydrocarbon chain, often a long chain of $-CH_2-$ groups. For many surfactants the nonpolar tail would be much longer than indicated in the cartoon. The final frames of the cartoon show how the polar head remains in the water and the nonpolar tail is forced out of the water solution.

SURFACTANTS

e) uses of surfactants

Surfactants have many applications. One kind can stabilize the foam in beer, where foam is a desirable thing, while another kind can break the foam in a chemical process, where foam causes problems. Emulsifiers prevent mayonnaise from breaking down into a layer of oil and a layer of water and prevent peanut butter from settling and leaving a big layer of oil at the top of the jar. But probably the most familiar example of surfactant use is in detergents. The cartoon shows the surfactant molecules attaching their nonpolar tails to a droplet of oil and incorporating the droplet at the center of a cluster of detergent molecules (called a **micelle**). Dirt

sticks to cloth because of a layer of oil. To clean the cloth we use a surfactant. The surfactant incorporates the oil into a micelle and the dirt falls away from the fabric.

ADHESIVES

f) a sticky problem

The first requirement of an adhesive is that it form a reasonably strong bond with the atoms on the surfaces of the objects that are to be glued together. It must be understood that the surfaces to be bonded must be clean. Formerly, different kinds of glues were used to bond different kinds of materials; this is still true to a great extent. However, today there are adhesives that will bond almost any material to any other.

The interview with Al Pocius provides some insight into the challenges that confront the surface chemist when a new adhesive is under development. Anyone who knows what the first transparent tape was like (It mainly stuck to itself--getting a piece off the roll was an accomplishment.) and compares it with the transparent tape on the market today can appreciate Al Pocius's remarks.

CATALYSTS

g) graphic of diatomic molecules on a catalyst surface

The cartoon shows two different kinds of diatomic molecules breaking apart into atoms which migrate over the surface, they finally change partners and then come off the surface as a new substance. This is one way by which a catalyst could produce a reaction. Another way would be for one molecule to break apart while the other simply sits down on the surface and reacts with the fragment from the first molecule. Clearly there are a number of variations that could occur, but all of them involve the making and breaking of bonds at the surface of the catalyst.

h) Madey interview; modelling and measurements

The interview with Ted Madey of the National Bureau of Standards provides a nice example of the use of models: the iron crystal with the layers of iron atoms, the ammonia molecule and fragments from it located in various positions on the model. Then there is the experiment, electron bombardment of an iron surface having ammonia adsorbed on it, resulting in the emission of beams of protons from the ammonia molecule. The spinning ammonia molecule gives a proton emission that looks like a halo-like cloud. An $-NH_2$ fragment frozen in position yields two distinct proton emission clouds. It is a beautiful example of the interplay of modelling and experimental work.

Note: In 1988 The National Bureau of Standards (NBS) was renamed; it is now The National Institute of Standards and Technology (NIST).

l) acrylonitrile

The acrylonitrile story is a good example of serendipity. The researchers were trying to design a catalyst that would partially oxidize propane, thereby making it more reactive and consequently more useful. It didn't work. So they decided to see if it would work with propylene, a more reactive gas. They added some ammonia, which often aids the action of this type of catalyst. It still didn't do what they wanted, but it produced a quite different and useful result. From propylene and ammonia, they made acrylonitrile in one step.

$$\underset{\text{propylene}}{H_2C{=}CHCH_3} + \underset{\text{ammonia}}{NH_3} \longrightarrow \underset{\text{acrylonitrile}}{H_2C{=}CHCN} + \text{hydrogen enriched gas}$$

As Jeanette Grasselli points out, the economic consequences of this discovery were enormous.

SURFACE AREA

j) shapes of catalyst particles

The picture shows catalyst material made in various shapes and particles of various sizes. It must be borne in mind that a heterogeneous catalyst is more effective the greater the surface area per gram. The surface area per gram is greatest if the catalyst is in the form of a very fine powder. But a powder may be difficult to use industrially; it may be hard to separate from the mixture after the reaction is over, for example. So the fine powder is often formed into small pellets or the macaroni-like tubes shown in the program. But these shapes are made to be very porous and spongy so that there is much more surface available than is evident to the naked eye. The reaction can take place on surfaces in the interior of the pellets, for example.

k) surface area demonstration

In this demonstration, Don Showalter uses the same material but in two different forms. One sample of the powder has been compacted under high pressure using a hydraulic press. The surface area of this sample is simply the external geometric area that is apparent to the eye; the pellets are not porous or spongy. When these pellets are put in water there is no obvious change.

The second sample of the same material is the finely divided powder. When this sample is stirred into water, the water forms hydrogen bonds with all the -OH groups on the backbones of the starch molecules that are exposed on the surfaces of all these tiny grains of powder. All of the water gets bound up in a stiff gel by the starch granules. The reaction is dramatic; the gel is formed almost instantly.

Take note that you have probably seen something very similar before. It just wasn't as dramatic. When you make the filling for a lemon pie, a little corn starch is added during the cooking. It takes a minute or so for the gel to form, so the effect is not so startling as in the demonstration. The setting of gelatine is the same kind of phenomenon. Gelatine takes a relatively long time to form the gel.

l) zeolites

The zeolites are a rather different type of material. Whereas the industrial catalysts we described above are porous and spongy because the grains have been only packed rather loosely and there are holes between the individual grains. In the zeolites the molecular structure itself has holes and pores in it. This is evident in the model shown by Edith Flanigen. These zeolites have the ability to take molecules out of the reaction mixture, or sometimes they can hold the molecule in a special orientation so it can react in a certain way. They form a class of very special catalysts.

HANDS ON

1. *Take a tablespoon of cornstarch and stir it into half a cup of cold water. Observe what happens. Heat the mixture gently in a saucepan for a few minutes and observe. Fiddle with the proportions to find the least amount of corn starch that will set to a gel in half a cup of water.*

2. *Consider the catalytic converter in your car. Inside it, there is a mass of catalyst material having a very large surface area. On the surface of this catalyst, the unburned gases from the engine are burned to carbon dioxide and water. Nitrogen oxides are decomposed to nitrogen and oxygen. All these reactions are exothermic. Read the users manual for your car; you are warned not to park the car over high grass or other combustible materials. The converter gets hot enough to set them on fire.*

QUESTIONS

1. *Water boils at 100 °C and ether at 34 °C. Which of these liquids will exhibit more pronounced surface effects?*

2. *If hydrogen is passed over finely divided, warm platinum oxide, the oxide is reduced to metallic platinum. Why would this method be preferred to grinding metallic platinum if the product is to be used as a catalyst?*

3. *Suppose you could shrink to atomic size and managed to get inside of a pellet of a catalyst. What would the interior of the catalyst look like?*

4. *Why do people in the cold parts of the country coat their metal snowshovels with paraffin wax?*

5. *What evidence is there that neutral molecules and atoms exert attractive forces on one another?*

UNIT 21

CARBON

BEFORE WATCHING

YOU ALREADY KNOW

Covalent bonding.

Cis-tran isomers.

READ

Chapter 12: The Ubiquitous Carbon Atom—An Introduction to Organic Chemistry (entire chapter)

Chapter 13: Organic Chemicals: Energy and Materials for Society (entire chapter)

OVERVIEW

This program emphasizes the central importance of carbon chemistry to the organic world. It points out that carbon is unique in the variety of compounds that it can form.

The basic types of bonds that carbon forms are described, and examples of structural isomerism are given. The large numbers of possible structural isomers are shown for a few relatively small molecules to convey, in a simple way, why carbon can form such a huge variety of compounds.

The use of functional groups to systematize carbon chemistry is described, and several examples of functional groups are given. The use of esters as components of flavors and fragrances is presented through an interview with a flavor chemist.

A simple synthesis of a compound, aspirin, is demonstrated.

The program concludes with interviews with a natural products chemist and with the head of a chemical company.

WHAT TO LOOK FOR

DIVERSITY OF CARBON CHEMISTRY

a) carbon chemistry is unique

KINDS OF BONDS

b) single bonds
c) double and triple bonds

ISOMERS

d) structural isomerism

FUNCTIONAL GROUPS

e) examples
f) flavors and perfumes

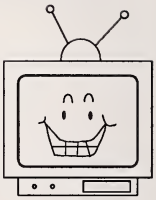
SYNTHESIS

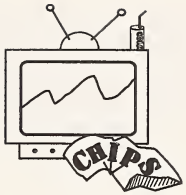
g) aspirin
h) art imitates Nature

CHEMICAL INDUSTRY

i) magnitude of the operation

WATCH THE PROGRAM





AFTER WATCHING

DIVERSITY OF CARBON CHEMISTRY

a) Carbon chemistry is unique.

The narration points out that all living organisms are based on carbon compounds. The other elements, hydrogen, oxygen, and nitrogen, are equally necessary, but the parent compound of all these molecules is a carbon compound.

There are several reasons for carbon's ability to form such a wide variety of compounds.

1. The ability to form chains

Carbon is the only element that can form stable molecules in which many carbon atoms are bonded to one another to form a chain or rings. The ability of other atoms to form chains or rings is usually limited to chains or rings with no more than three or four atoms, occasionally the number goes as high as eight. But with carbon, as far as we know, there is no limit to the number of atoms that can be in a chain.

2. The strength of the bonds

Carbon has the ability to form bonds with many other atoms as well as with itself. If we look at the strength of these bonds we find that they are all rather strong bonds, but one does not differ greatly from another in strength. This means that there is no great tendency for carbon to form only bonds with one element in preference to another.

If we contrast this with the behavior of silicon, for example, we find that the bond between silicon and oxygen is very much stronger than that between silicon and any other atom except fluorine. The bond between silicon and fluorine is much stronger than that between silicon and oxygen. Now, in the earth's crust oxygen is common and fluorine is relatively rare so that the only naturally occurring compounds of silicon are silicates, compounds which involve silicon-oxygen bonds.

3. The size of the carbon atom

The carbon atom is in the first period of eight in the periodic table. This has two consequences: first, the atom is one of the smallest atoms and second, it can form four bonds and **no more than four bonds.** The size and the limitation to four bonds means that in most circumstances there is no kinetic pathway to convert one carbon compound to another. Almost all the reactions in organisms require special catalysts, enzymes, to provide this kinetic pathway.

Again we make a brief comparison with silicon. Silicon is in the second period of eight in the periodic table. The silicon atom is somewhat larger than the carbon atom, but, more importantly, it can form up to six bonds if presented with a suitable partner. Thus, if an oxygen molecule approaches a SiH_4 molecule there is room for the oxygen to form a bond with the silicon atom; this strong silicon-oxygen bond loosens the silicon-hydrogen bonds, and the hydrogen atoms are converted to water and the silicon to silicon dioxide. SiH_4 bursts into flame spontaneously on contact with air. CH_4 is stable in air; the oxygen molecule cannot get at the carbon atom to form a bond. To burn CH_4, we must remove a hydrogen atom from the molecule to give the oxygen molecule an entrance to form a bond with the carbon atom. We can remove the hydrogen atom by passing a spark through the gas or by heating it in a flame (touching a match to it).

4. The ability to form multiple bonds

Although there are some exceptions to the rule, generally speaking we can say that multiple bonds are formed only by the elements in the first period of eight in the periodic system. Thus, carbon can form double and triple bonds with other atoms in the first period of eight--usually carbon, nitrogen, and oxygen atoms. The ability to form multiple bonds provides another way to diversify the compounds that can be formed and a way to enhance their reactivity, since multiply-bonded structures can undergo reactions that are not possible if only single bonds are present.

Thus, carbon dioxide is a discrete molecule having two double bonds in it: $O{=}C{=}O$. In contrast, silicon dioxide can only form single bonds to oxygen; as a result silicon dioxide is a macromolecule in which every silicon atom is surrounded by four oxygen atoms and every oxygen atom is connected to two silicon atoms.

KINDS OF BONDS

b) single bonds

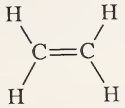
The carbon atom can form four bonds. The simplest type of carbon compound is one in which the carbon atom is bonded to four neighbors of the same kind; e.g., methane, CH_4. The four bonds are called single bonds; these bonds are directed to

the apices of a tetrahedron. The bonded atoms need not all be the same. In ethane, C_2H_6, each carbon atom is bonded to three hydrogen atoms and to one carbon atom. Each carbon atom is bonded to four neighbors; this is the maximum number of neighbors the carbon atom can have, so the carbon atom is said to be saturated. If all the carbon atoms in a molecule are bonded to four neighbors the molecule is called a saturated molecule.

c) double and triple bonds

If the carbon atom is bonded to fewer than four atoms, then the molecule is called an unsaturated molecule.

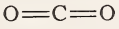
If the carbon atom is connected to three other atoms, these three atoms lie at the corners of a triangle; two of the three are singly bonded to other atoms and the third is connected by a double bond; an example is ethylene.



In this molecule, the triangles around the two carbon atoms lie in the same plane so that all the atoms in this molecule lie in the same plane.

If the carbon atom is bonded to only two other atoms, the carbon atom and its two neighbors lie on a straight line. This molecular geometry can happen in two ways, by the carbon atom forming a single and a triple bond, as in acetylene:

or by the carbon atom forming two double bonds, as in carbon dioxide:



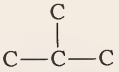
Both of these molecules are linear.

ISOMERS

d) structural isomerism

Molecules with the same molecular formula in which the atoms are arranged differently are called structural isomers. The simplest example is given by butane and isobutane. The carbon skeletons are:

butane



isobutane

Clearly the arrangements are different. In isobutane one carbon atom is connected to three other carbon atoms, while in butane the carbon atoms are connected at most to two other carbon atoms.

As the number of carbon atoms in the compound increases, the number of possible isomers goes up very rapidly. There are 18 possible isomers for octane, which has the molecular formula C_8H_{18}. The octanes collectively are a major component of gasoline. For a hydrocarbon with 20 carbon atoms there are over 366,000 possible isomers.

FUNCTIONAL GROUPS

e) examples

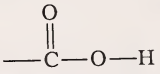
The hydrocarbons are compounds containing only hydrogen atoms and carbon atoms. In the saturated hydrocarbons all of the carbon atoms are bonded to four neighbors. These compounds are called paraffins (from Latin: *parum* meaning "too little" and *affinis*, meaning "akin"). They are so named because they are chemically rather inert. We have to use extreme conditions to get them to react with anything. The most common reaction that they undergo is combustion; even in this case we have to provide an initiating event (touch a match to them) to get them to burn.

If we introduce a double bond (or a triple bond) somewhere in the molecule, there will be several types of reactions that can occur that were not possible with the paraffins. These reactions are characteristic of the double (or triple) bond. A double bond or triple bond is the simplest example of a **functional group**. A functional group is a group of atoms in a molecule that are bonded in a particular way. The functional group enables the molecule to undergo certain chemical reactions that are characteristic of the functional group.

The hydroxyl group, -OH, is another example of a functional group. If it replaces a hydrogen of a hydrocarbon, the molecule is called an alcohol. For example, if one of the hydrogen atoms in ethane, C_2H_6, is replaced by an -OH group we get ethyl alcohol, C_2H_5OH.

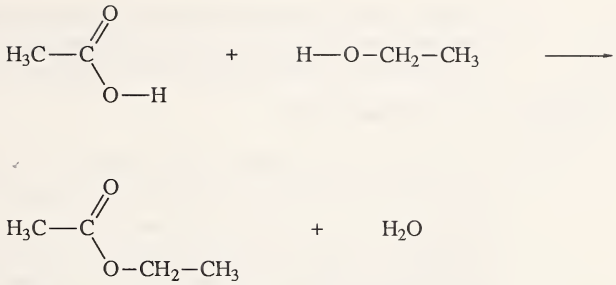
Glycerin is another common alcohol; it contains three -OH groups.

The carboxyl group, -COOH, or



placed in a molecule makes it an acid. If we replace one $-CH_3$ group in ethane by -COOH we get acetic acid, CH_3COOH. Vinegar is a dilute solution (about 5%) of acetic acid in water.

It is possible to react an alcohol with an acid, eliminate a molecule of water, and produce a compound called an ester. Thus,



The reaction of acetic acid with ethyl alcohol produces the ester, ethyl acetate, a fragrant liquid.

The natural fats and oils, described in Program 9, are esters. Glycerine is the alcohol (three -OH groups) and the acids are long chain acids such as stearic acid, $C_{17}H_{35}COOH$. Glyceryl stearate is a major component of beef fat.

f) flavors and perfumes

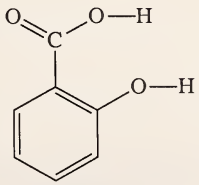
Natural fragrances and flavors are often esters. Oil of wintergreen, for example, is methyl salicylate, the ester of methyl alcohol and salicylic acid.

The flavor industry and the perfume industry described in the program provide two unusual examples of applied chemistry.

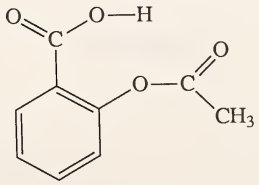
SYNTHESIS

g) aspirin

Salicylic acid is a compound that has two functional groups. It consists of a benzene ring in which one position is occupied by a carboxyl group, so it is an acid, and another position is occupied by a hydroxyl group, so it is also an alcohol. The reagent acetic anhydride, is used to convert the alcohol group to an ester. The relation between the composition and structure of salicylic acid and acetylsalicylic acid (aspirin) can be seen by examining the two structures:



salicylic acid



acetylsalicylic acid

Aspirin is one of the early successes of the pharmaceutical industry. It is one of the first medicinal products to be produced synthetically in large amounts. Since it was first produced in 1899, it has been in heavy demand as an analgesic and antipyretic.

h) Art Imitates Nature

Willow bark was a pain killer. Chemists found that the active substance was salicylic acid. They then improved the product by converting the salicylic acid to aspirin.

Kathlyn Parker is involved in much the same process with plant materials useful as medicinals. The plant extract is checked for any medicinal activity. Then the active substance is isolated from the extract. The substance is analyzed, and its structure determined. It may be marketed as a natural material or, if it is feasible, it may be manufactured as a chemical product. Chemically related compounds are synthesized and tested to see if they may be more effective, or have fewer side effects, or have other advantages over the natural material. Again, the process involves checking what Nature does, imitating it, and, where possible, improving on it.

CHEMICAL INDUSTRY

i) magnitude of the operation

When we observe the test tube synthesis of aspirin on a semi-micro scale, it is difficult to remember that more than 10,000 tonnes of aspirin are synthesized each year in the United States alone. In Don Showalter's synthesis of aspirin, the waste material, chemically equivalent to a bit of vinegar and a bit of a soft drink, can be safely disposed of by pouring down the drain. On the other hand, the waste products from many industrial processes are not as innocuous as those from this laboratory aspirin synthesis, and the amounts formed are measured in thousands of tonnes.

Mary Good, a distinguished industrial chemist, describes the new emphasis that is being put on minimizing waste in the chemical industry. She also points out that a large proportion of the population is either directly or indirectly dependent on the chemical industry.

HANDS ON

1. *Go to your spice rack and sniff the fragrances of the various spices. Vanilla flavor and almond flavor are often artificial flavors. Check the list of*

ingredients to see if you can identify the ester or alcohol that is the main flavoring substance.

QUESTIONS

1. *Why are there so many different carbon compounds?*

2. *Why is CO_2 a gas while SiO_2 is a solid?*

3. *a) Draw all the isomers of pentane, C_5H_{12}.*

   b) Butene, C_4H_8, has one double bond between two carbon atoms. Draw all the isomers of butene.

4. *Name four functional groups, and draw their structures.*

5. *Name one class of compounds that is responsible for the fragrance of flowers and fruits.*

UNIT 22

THE AGE OF POLYMERS

BEFORE WATCHING

YOU ALREADY KNOW

Carbon atoms form single, double, and triple bonds with other carbon atoms and with other kinds of atoms.

Carbon-based compounds may have straight or branched chains, as well as cyclic structures.

Catalysts make reactions go in a reasonable time.

The molecular structure of a compound dictates its macroscopic properties.

READ

CHAPTER 14: Man-made Giant Molecules—The Synthetic Polymers
(entire chapter)

OVERVIEW

The program begins with examples of the many different kinds of polymers and the many different uses to which they are put today. We make everything from automobile bodies to replaceable parts for our own bodies from polymers.

The winning of materials from petroleum through the processes of fractional distillation and cracking is presented. In particular it is pointed out that ethylene, obtained from petroleum, is one of the most important raw materials for the polymer industry.

The mechanism of the polymerization of ethylene to form polyethylene is illustrated. Note that the ethylene molecule itself is the *monomer* (From Greek: *mono* meaning "one" and *mer* meaning "part") and the polyethylene is the *polymer* (From Greek: *poly* meaning "many"). So, a polymer has "many parts"; it consists

of many of the monomer units. In the example shown, the polyethylene consists of many ethylene residues strung into a long chain.

The effect of different structures on the macroscopic properties of the polymer is illustrated by polyethylene film, bottles, and bottle caps.

The effect of making substitutions in the ethylene molecule before polymerizing it is shown by the examples of styrene and acrylonitrile from which we get polystyrene ("Styrofoam") and polyacrylonitrile ("Acrilan" or "Orlon"). Teflon is another example but is not shown in the film.

WHAT TO LOOK FOR

POLYMERS ARE EVERYWHERE

a) different kinds of polymers

SYNTHESIS OF POLYETHYLENE

b) ethylene from crude oil
c) polymerization

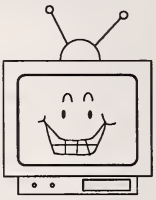
KINDS OF POLYETHYLENE

d) structure and properties
e) the soda bottle

DIFFERENT MONOMERS

f) substituted polyethylenes
g) polyacetylene

WATCH THE PROGRAM



AFTER WATCHING

POLYMERS ARE EVERYWHERE

a) different kinds of polymers

There are so many polymers used for so many things that it is almost impossible to give an adequate account of the subject. We content ourselves here with just a few examples.

There are many important and useful natural polymers; for example,

hydrocarbons: rubber;

proteins: silk, wool, leather, casein, enzymes, and many others;

carbohydrates: cellulose (wood, cotton, paper), starch, glycogen (glycogen is the polymeric carbohydrate the animal body uses for energy storage);

polynucleotides: DNAs and RNAs.

Among artificial polymers, probably the first to be synthesized was polystyrene in 1839; but 100 years would pass before polystyrene was put to any use. Celluloid was the first plastic used. In 1868 celluloid was prepared by nitrating cellulose and mixing the product with camphor. Another polymer, Bakelite, was a result of a chemical reaction (between phenol and formaldehyde) gone wrong, but the inventor, Baekeland, rescued what appeared to be a hopeless mess and made a useful product out of it. One more example of serendipity in science and technology! Bakelite was the forerunner of the modern phenolic resins.

Rayon was developed at the turn of the century.

Systematic polymer chemistry had its beginning in the 1920s with Staudinger in Germany. In 1929 Wallace Carothers at the Dupont Co. began his pioneering work on the synthesis of polymers from known, simple molecules. This led to the invention of a number of important polymers, including nylon. The outbreak of World War II led to an enormous effort in polymer chemistry, particularly in the attempts to produce a suitable synthetic rubber. By the end of the war in 1945, the technology was in place to produce many different kinds of polymeric materials.

Today polyethylene is the world's most common synthetic polymer.

SYNTHESIS OF POLYETHYLENE

b) ethylene from crude oil

Polyethylene is made from ethylene, which in turn is obtained from petroleum. Crude oil is the basic feedstock for the petrochemical industry from which all the many blessings of our polymer age flow. Crude oil itself is a dirty mixture of hundreds of carbon compounds. We use a process called fractional distillation to separate crude oil into useful materials.

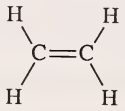
Fractional distillation is done in a giant column packed with pieces of ceramic material. The column is heated at the bottom but is cool at the top. The temperature decreases in a regular way from the bottom to the top of the column. The crude oil is heated and then is injected into the column at a height where the temperature is even hotter than that of the hot oil.

The low molecular weight hydrocarbons in the oil vaporize and move upward in the column. The heavier hydrocarbons remain as liquids and move downward in the column. The process is controlled by the temperature pattern in the column. The vapor from low boiling substances moves upward as the high boiling liquids flow downward in the column. This countercurrent flow of liquid and vapor in the tower produces a kind of equilibrium between liquid and vapor. At each position in the tower, equal amounts of liquid and vapor evaporate and condense, respectively. By draining off liquid at different heights in the column, liquids of different properties are obtained. Low boiling mixtures, gasoline and kerosene, are obtained from positions near the top of the column and high boiling substances, oils and greases, from positions near the bottom. Heavy carbonaceous materials such as tar and asphalt collect at the bottom of the column.

Once the crude oil is separated into "fractions" by distillation, the various fractions are treated so that we can produce the things we need in greater quantity. For example, we can take the heavier oils and crack them into smaller molecules so as to produce a greater amount of gasoline. To make ethylene we subject even the light fractions to additional cracking.

c) polymerization

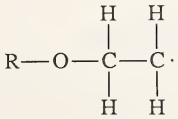
Ethylene is a very simple molecule consisting of two carbon atoms, connected by a double bond, and four hydrogen atoms; two hydrogen atoms are bonded to each carbon atom.



These molecules can polymerize if we introduce an organic peroxide, R-O-O-H. This molecule breaks into two fragments, each with an unpaired electron; such a fragment with an unpaired electron is called a free radical.

$$R—O—O—H \cdots\cdots R—O\cdot \quad \text{and} \quad \cdot OH$$

When one of the free radicals comes near an ethylene molecule, it opens the double bond and we get



This in turn can react with another ethylene molecule, and so on and on. Ultimately, a very long chain molecule is built up, as is shown in the program. Because of the way in which the reaction is initiated this is called a free radical chain reaction polymerization. Ordinarily, thousands of units are added to the chain before the reaction terminates.

KINDS OF POLYETHYLENE

d) structure and properties

The program demonstration shows differences in properties between different kinds of polyethylene. If the polymerization is done in such a way as to encourage the growth of side branches on the polymer, then the individual polymer molecules do not pack together very well; the polymer has a low density. The molecules are like a bunch of felled trees; the branches push the trees apart. If we pull on the sheet, it stretches and ultimately breaks. This material makes the "wrap" that we use in the supermarkets and in the kitchen to wrap food.

On the other hand, if the polymerization produces molecules without side branches, then they pack together closely; the polymer has a high density. This is the polyethylene from which the milk bottle is made. It is relatively tough and hard to pull apart.

If we bond individual polymer molecules to one another, the structure is said to be cross-linked. The entire sample becomes essentially one huge molecule and is very tough and difficult to break or bend. The polyethylene cap on the milk bottle is an example, as are the ropes in the hammock and the artificial plastic ice.

e) the soda bottle

In designing the soft drink bottle, Nathaniel Wyeth had the idea of building the bottle using sheets of plastic that are turned 90° to one another. Note that this

implies that when the sheet is cast there is a "machine" direction. Imagine the molten plastic coming through a set of rollers and solidifying as it emerges. The tensile strength of the plastic sheet will be different in the machine direction (the direction perpendicular to the axis of the rollers) and in the direction parallel to the rollers. One direction is weak. If we use two sheets at 90° the weak direction is eliminated. The same principle is used in making plywood.

DIFFERENT MONOMERS

f) substituted polyethylenes

By replacing one or more of the hydrogens in ethylene with some other group of atoms, we can produce polymers with different properties.

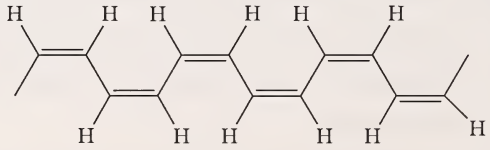
If one of the hydrogen atoms in ethylene is replaced by a benzene ring, the resulting monomer molecule is styrene. The brilliantly clear cups used at parties are made of polystyrene. This polymer is rather brittle. Foamed polystyrene is produced by blowing air or other gas through the molten polymer or releasing a gas by a chemical reaction. The polystyrene foam is used as an insulating material in buildings and in cups for hot liquids. The trapped gas in the foam makes the material an excellent insulator.

Replacing a hydrogen in ethylene by a -CN group yields acrylonitrile. When this is polymerized, we get polyacrylonitrile, with commercial names like Acrilan and Orlon. This material can be spun into tough fibers that are used to make carpets. The toughness of this polymer, compared to the relative softness of polyethylene, is a consequence of the polar -CN group that strengthens the attractive forces between the polymer molecules.

g) polyacetylene

Acetylene has a triple bond:

When this molecule is polymerized, a double bond remains between each pair of carbon atoms. The chain looks like this:



Note the chain of carbon atoms, with the alternating double and single bonds between them. We could equally well have drawn the structure with the positions

of the double and single bonds interchanged. How do we know which is correct? Nature is ahead of us here; the actual structure is a **hybrid** of the two. The bonds in the chain are neither double nor single but all have 50% double bond character. This means that the electrons that compose the double bonds are delocalized and can move freely over the entire length of the chain. As a consequence of this delocalization, the molecule itself can conduct an electrical current along its length.

HANDS ON

1. *Make a list of as many items as you can that are part of your car and are polymers. Include both carbon-based polymers and polymers based on other elements.*

QUESTIONS

1. *What is the raw material from which most polymers are made?*
2. *What happens in the fractional distillation of crude oil?*
3. *Why is it necessary to "crack" petroleum fractions?*
4. *Define the terms: monomer; polymer.*
5. *Describe what happens in the process of polymerization.*
6. *The polymer, Teflon (polytetrafluoroethylene), is made by polymerizing ethylene in which all the hydrogen atoms have been replaced by fluorine atoms. Sketch a portion of the polymer chain that contains six carbon atoms.*

UNIT 23

PROTEINS: STRUCTURE AND FUNCTION

BEFORE WATCHING

YOU ALREADY KNOW

Bonding in organic molecules.

Chirality.

Polymers.

READ

Chapter 15: "Proteins"; "Enzymes"

Chapter 22. "Skin, Hair, Nails and Teeth - A Chemical View"; "Curling, Coloring, Growing, and Removing Hair"

OVERVIEW

The variety of proteins in the natural world is stressed. The fibrous proteins are tough materials, insoluble in water, that consist of polypeptide chains arranged along a single axis either in long fibers or sheets. The fibrous proteins are suitable structural material for muscle, nails, hair, etc. The globular proteins consist of polypeptide chains that are folded into relatively compact spherical or globular structures. These proteins are soluble in water and are mobile in water. Enzymes, the catalysts that run the body as a chemical factory, are globular proteins. Other globular proteins include antibodies, some hormones, and transport proteins such as hemoglobin.

Three levels of protein structure are described. The primary structure is the sequence of amino acid residues in the protein. The secondary structure is the alpha-helix or the beta-sheet. The tertiary structure is the way the protein finally folds together on itself.

The program concludes with a description of a model for enzyme action. The uniquely shaped "dock" allows the enzyme to accept only molecules with the proper chirality. It rejects the mirror image molecules. The application of this model to the development of enzyme blockers is described.

WHAT TO LOOK FOR

OCCURRENCE

a) as structural elements of organisms
b) as functional elements of organisms
c) variety of proteins

STRUCTURE

d) amino acid sequence
e) alpha-helix
f) hair styling
g) beta-sheet

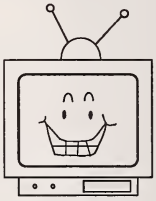
TERTIARY STRUCTURE

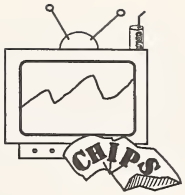
h) examples

ENZYMES

i) mechanism
j) blockers

WATCH THE PROGRAM





AFTER WATCHING

OCCURRENCE

a) as structural elements of organisms

The proteins that are most familiar to us are the structural proteins, such as wool, hair, silk, the proteins that compose beaks, muscles, and fingernails. These proteins are the substances that are responsible for the structure of the natural material in question. The alpha-keratin of hair consists of bundles of twisted strands of helical polypeptide chains.

b) as functional elements of organisms

Among the functional duties of proteins, certainly the most extraordinary and the most diverse is that of catalyzing chemical reactions in living cells. These protein catalysts are called **enzymes**. Without them we would simply die. We could not move; we could not breathe; we could not eat; we could not metabolize food.

Other functions are: the transport of oxygen in the blood by hemoglobin, the transport of lipids (fats) in the blood by lipoprotein, and the regulation of glucose metabolism by insulin. These are only a few of the multitude of chores performed by proteins.

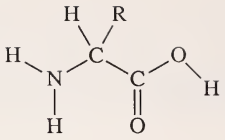
c) variety of proteins

There is a vast variety of proteins; the total number of different kinds of proteins in all living organisms has been estimated to be about 10^{12}. As large as this number is, it is much smaller than the number of possible protein molecules. Still, with only rare exceptions all the proteins we know about are composed of only 20 amino acids. Our first concern is how these amino acids are combined to form proteins.

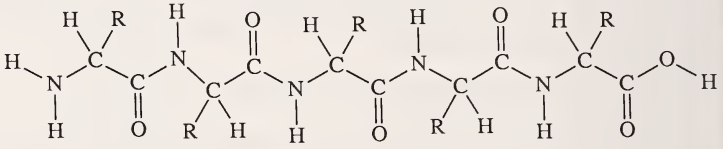
STRUCTURE

d) amino acid sequence

An amino acid is a carboxylic acid that has an amino group (an $-NH_2$ group) attached to the carbon atom next to the carboxyl group (called the "alpha carbon atom").



One amino acid differs from another by having a different group, the group designated by R in the diagram, attached to the alpha carbon atom. When water is eliminated between two of these amino acids, a peptide bond is formed. Repetition of this process produces the backbone common to every protein, the polypeptide chain.



The **primary** structure of any protein is described by the sequence of amino acid residues in the protein. Imagine that you have twenty bins, each filled with beads. All the beads in any one bin have the same color, but the beads in different bins have different colors. We pick out beads randomly from the bins and put them together on a string. The sequence of colors in the string is analogous to the sequence of amino acid residues in a peptide.

To get some idea of the number of ways the amino acids can be arranged, suppose we construct a string of beads with twenty beads on it. There are twenty ways (twenty bins) of choosing the first bead and there are twenty ways of choosing the second bead, so there are a total of 20 x 20 = 400 ways of choosing the first two beads. There are 20 ways of choosing the third bead and each of these can be combined with any of the 400 combinations of the first two beads. Thus, there are 400 x 20 = 8000 ways to produce a string of three beads. For a string of twenty beads there are $20^{20} = 1.05 \times 10^{26}$ possibilities. A protein with only twenty units is a very small protein indeed; it has a molar mass of only about 2400. The molar masses of proteins range from about 5000 for very small proteins to over 1,000,000 for large proteins. More common figures for molar masses are from 50,000 to hundreds of thousands. Nature apparently does not synthesize anywhere near the number of different proteins that are possible. Some of the possibilities may have appeared and then disappeared through the operation of natural selection.

e) alpha-helix

Once the primary structure, the amino acid sequence, is established, the protein can coil up to form a secondary structure, the alpha-helix, by forming hydrogen bonds between amino acids in the chain. Linus Pauling's discovery of the alpha-helix configuration in proteins was one of the great advances in biochemistry. It should be pointed out that not all proteins can form the alpha-helix structure; it depends on the side groups, their size, and polarity.

f) hair styling

A rather far-out illustration of the macroscopic properties that result from the alpha-helix is provided by the properties of hair and by hair styling.

The hair fibril is built up by taking either three or seven polypeptides in the alpha-helix configuration and twisting them together. This composite molecule is held together by disulfide bonds that form between the individual alpha-helices. The sulfide groups are present in cysteine, one of the twenty amino acids found in proteins. So, sticking out of two polypeptide chains we occasionally find the -SH groups of a cysteine residue. Thus, we can have

$$\begin{array}{ll} -S-H & H-S- \\ -S-H & H-S- \\ -S-H & H-S- \end{array}$$

These groups can be oxidized to yield disulfide bonds:

$$\begin{array}{l} -S-S- \\ -S-S- \\ -S-S- \end{array}$$

These disulfide bonds hold the two polypeptide chains together in the hair fibril. The disulfide bonds can be opened by a reducing agent, and the two alpha-helices can move relative to one another when the hair is curled into the desired shape. An oxidizing agent is then used to reform the disulfide links. These newly formed bonds hold the hair in its curled condition.

g) beta-sheet

The beta-sheet is an example of a different kind of secondary structure. In the beta-sheet there are no hydrogen bonds between the atoms within a given polypeptide chain; the hydrogen bonds are formed between adjacent polypeptide chains. A large number of these chains are lined up parallel to each other to form an extended sheet. This sheet structure is the one found in silk fibroin, the silk protein. It is found that certain amino acids in the polypeptide chain tend to destabilize the alpha-helix. One of these amino acids is glycine. Since about half

the amino acid residues in silk are glycine it is understandable why the helix does not form.

TERTIARY STRUCTURE

h) examples

The computer models of proteins shown in the program illustrate the tertiary structure of proteins.

One example given is that of myoglobin, which has several sections of alpha-helix, but the entire molecule is bent in a number of places so that, overall, it is globular. Proline, an amino acid that cannot incorporate into an alpha-helix, is present at the bends of the chain and interrupts the alpha-helix structure.

Flavodoxin, an enzyme, has both the alpha-helix and the beta-sheet structure in portions of its secondary structure. Again, the molecule folds up to yield a globular tertiary structure. The secondary structures reflect the kinds of amino acids present in those portions of the polypeptide chain.

ENZYMES

i) mechanism

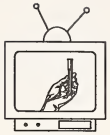
In living cells, enzymes catalyze all the chemical reactions that are required for the functioning of the organism. As catalysts, enzymes increase the rate of chemical reactions in the cells. It is important to note that a given enzyme does not catalyze all chemical reactions but only a particular reaction (or class of reactions). The reason for this specificity has long been an object of speculation. The current model supposes that the enzyme looks like an oddly shaped dock. One of the reactant molecules fits into this dock, and by fitting into the dock is able to react. This model also can explain why an enzyme can only catalyze the reaction of one optical isomer and not the other.

j) blockers

An "enzyme blocker" is a molecule that will tie up the active site on an enzyme. This prevents the enzyme from catalyzing the reaction. The program gives the example of a blocker that prevents the enzyme, rennin, from producing too much of a substance that constricts the blood vessels.

It is clear that some caution is in order here. Cyanide ion is a powerful poison simply because it inhibits the action of a respiratory enzyme. The person cannot utilize oxygen and dies in a few moments.

HANDS ON



1. *Heat a pint of milk in a sauce pan until it is lukewarm. Remove from the heat, and pour in half a cup of vinegar while stirring constantly. The milk will curdle immediately. Continue stirring until the curd coagulates into a rubbery mass. Lift the mass out and squeeze it to remove the water. This product is casein, a milk protein. Casein is a constituent of cheese, of some paints, and of white glue. Other household examples of proteins are egg white, gelatin, and, of course, meats and beans.*

QUESTIONS

1. *What functional groups are present in an amino acid?*

2. *Describe the steps in the process of forming a polypeptide from a collection of amino acids.*

3. *Proteins are built from 20 amino acids. How many different proteins with 50 amino acid residues are possible?*

4. *Consider a molecule of the polymer, polyethylene, and a protein molecule as if they were strings of beads. How would the string representing polyethylene differ from that representing a protein?*

5. *Draw the structure of a portion of a polypeptide (3 or 4 residues).*

6. *Imagine a peptide which contains only 3 amino acid residues and that these three can be chosen from a set of only four amino acid residues, A, B, C, and D. Write down the amino acid sequences for all the peptides that could be made under these restrictions.*

UNIT 24

THE GENETIC CODE

BEFORE WATCHING

YOU ALREADY KNOW

Proteins have primary, secondary, and tertiary structures.

READ

Chapter 15: "Nucleic acids"

OVERVIEW

The program begins with a look at sickle cell anemia, a genetic disease. The structure of normal hemoglobin, a protein, is shown and the various levels of structure described. It is pointed out that sickle cell anemia results from a **single** error in the synthesis of a chain of 146 amino acid residues.

The composition of the DNA molecule is described, and the structure is illustrated. The role of DNA molecules as the "librarians" of the cell is brought out, and the significance of the base sequence in the DNA molecule emphasized.

The program concludes with a description of the genetic code and the synthesis of proteins. The synthesis of human insulin by the bacterium *E. coli* is presented as an example of recombinant DNA technology.

WHAT TO LOOK FOR

HEMOGLOBIN

a) function
b) structure

SICKLE CELL ANEMIA

c) the disease
d) the origin of the disease

DNA

e) composition
f) structure

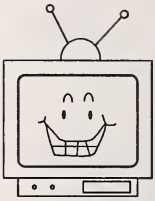
RNA

g) role in protein synthesis
h) genetic code

RECOMBINANT DNA TECHNOLOGY

i) human insulin

WATCH THE PROGRAM



AFTER WATCHING

HEMOGLOBIN

a) function

Certainly, if any protein can be characterized as a vital protein, hemoglobin can be. Localized in the red blood cells, hemoglobin combines with oxygen as the blood circulates through the lungs and carries the oxygen to all the parts of the body, where it is used in the metabolic processes. Any changes in the molecule that affect its ability to carry oxygen have serious consequences for the organism.

b) structure

The hemoglobin molecule consists of four polypeptide chains, each bonded to a heme molecule. Two of the four chains are 141 units long and have identical amino acid sequences. The other two are 146 units long and have identical amino acid sequences. The 141 unit chains are called the alpha-chains; the 146 unit chains are called the beta-chains. Some parts of the amino acid sequence are the same in the alpha- and beta-chains.

The secondary structure of the hemoglobin is described by the secondary structures of the polypeptide chains; that is, the amount of alpha-helix and beta-sheet in the chains. (Note that the terminology alpha-chain and beta-chain is simply a way of distinguishing between the two kinds of polypeptide chain in hemoglobin; it does not refer to the secondary structure. For example, both the alpha- and beta chains consist of about 70% alpha-helix interrupted by bends.)

The tertiary structure, as with any protein, refers to the way the polypeptide chain is folded upon itself. Both the alpha-chain and the beta-chain are folded into a globular shape.

The quaternary structure refers to the way the four polypeptide chains are assembled to form the complete hemoglobin molecule. The four globular units are put together in a roughly tetrahedral arrangement. This is the quaternary structure.

The oxygenation of hemoglobin produces changes in its quaternary structure. Upon oxygenation the beta-chains move closer together.

It must be emphasized that the primary structure, the amino acid sequence, contains the information that results in the secondary, tertiary, and quaternary structures.

SICKLE CELL ANEMIA

c) the disease

Sickle cell anemia is so-called because the red blood cells are shaped like a harvester's sickle instead of being flat and disc-like, as are the normal red blood cells. The sickle shape is a consequence of the abnormal hemoglobin molecules sticking together. These clumps of hemoglobin molecules cannot carry oxygen to the tissues; the person suffering from the disease has symptoms that result from this oxygen deficiency, as well as those resulting from the deformed red blood cells.

d) the origin of the disease

It has been discovered that the abnormal hemoglobin molecules that result in sickle cell anemia differ from normal hemoglobin molecules by **only one** amino acid residue in the beta-chain. Specifically, the first eight amino acid residues in the normal beta-chain are:

1	2	3	4	5	6	7	8	...	146
Val	His	Leu	Thr	Pro	Glu	Glu	Lys	...	His
					↑				
					Val				

The abbreviations Val, His, ..., and so on are used for the names of the amino acids. In particular, the glutamic acid (Glu) residue at position 6 is replaced by a valine (Val) residue in the abnormal beta-chain. The other 145 amino acid residues are the same and in the same order in both the normal and the abnormal molecules. The effect of this replacement is to replace a polar group with a nonpolar group. This changes the tertiary structure of the beta-chain. The net result is that the hemoglobin molecule cannot function properly.

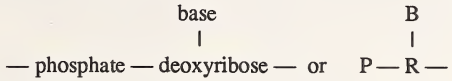
The gene that codes the amino acid sequence in the beta-chain of the sickle cell hemoglobin molecule is defective.

DNA

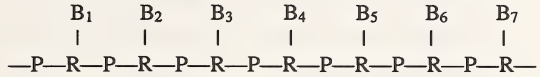
e) composition

The deoxyribonucleic acid (DNA) molecule contains the information for synthesizing proteins. The DNA molecule is a huge biopolymer; each unit of this polymer consists of a deoxygenated ribose residue attached to a phosphate group and one of four nitrogen-containing bases: adenine (A), cytosine (C), guanine (G), and thymine (T). This monomeric unit is polymerized into a giant molecule. One DNA molecule from an *E. coli* bacterium has a length of 1.2 mm and a molecular weight of 2.8 billion, for example.

The structure of the repeating unit can be drawn schematically as:



where the base can be any one of A, C, G, or T. The polymer looks like this:



f) structure

The polymeric molecule has a string of bases attached along its backbone. These bases can form hydrogen bonds with the bases on a complementary molecule of DNA. This pair of DNA molecules forms into the marvelous double helix. The hydrogen bonds holding the two DNA molecules together are formed in a special way: A bonds only with T, and C bonds only with G. Thus, the base pairings in the complementary strands might look like this:

Strand 1: ... A G T A A C T G ...
Strand 2: ... T C A T T G A C ...

It is this sequence of bases in the DNA molecule that codes the information that determines the amino acid sequence in protein synthesis. This is the genetic information that determines if we will have blue eyes or brown, and whether our hair will be black or blond. Our bodies are what our proteins make them. All of it is determined by the sequence of bases in the DNA molecule.

RNA

g) role in protein synthesis

Ribonucleic acid (RNA) differs from DNA in two respects. First, the sugar residue is ribose rather than deoxyribose, which has one less oxygen atom than ribose. Second, the four bases in RNA are A, C, G, and U (uracil). The uracil can form hydrogen bonds with adenine, just as the thymine in DNA does.

Protein synthesis needs a set of instructions for the amino acid sequence. This set of instructions is provided by the DNA. The portion of a DNA molecule that describes a complete polypeptide chain is called a **gene**.

The first step in protein synthesis is the transcription of the base sequence in the DNA molecule to the complementary base sequence in a **messenger RNA** (mRNA) molecule. The two strands might look like this:

DNA sequence	A G T A A C T G...
mRNA sequence	U C A U U G A C...

In the RNA, the U is the complementary base for A. After the mRNA has been synthesized using the DNA molecule as a template, the mRNA moves to the ribosomes, where protein synthesis takes place in the cell.

h) the genetic code

The genetic code is the sequence of bases in the DNA molecule. This sequence is transcribed in a unique way into a corresponding sequence in the mRNA molecule. This messenger RNA molecule carries the instructions to the site of protein synthesis. The genetic code has been deciphered to the extent of knowing that the code word for a given amino acid residue consists of a sequence of three bases on the RNA molecule.

We can ask the question, "How many ways can three bases be chosen from the four possibilities, A, C, G, U?" The first base can be chosen in four ways:

U	C	A	G

For each choice of the first base there are four ways to choose the second:

UU	CU	AU	GU
UC	CC	AC	GC
UA	CA	AA	GA
UG	CG	AG	GG

This means that there are sixteen possibilities. Note that sixteen pairs are too few to code for 20 amino acids.

For each of the 16 choices of the two bases there are four choices for the third base, making a total of 64 triplets.

UUU	CUU	AUU	GUU
UUC	CUC	AUC	GUC
UUA	CUA	AUA	GUA
UUG	CUG	AUG	GUG
UCU	CCU	ACU	GCU
UCC	CCC	ACC	GCC
UCA	CCA	ACA	GCA
UCG	CCG	ACG	GCG
UAU	CAU	AAU	GAU
UAC	CAC	AAC	GAC
UAA	CAA	AAA	GAA
UAG	CAG	AAG	GAG
UGU	CGU	AGU	GGU
UGC	CGC	AGC	GGC
UGA	CGA	AGA	GGA
UGG	CGG	AGG	GGG

The 64 base triplets, or **codons**, are sufficient to provide code words for the twenty amino acids. Of the 64 codons, 61 code for amino acids; each of these 61 codons corresponds uniquely to one amino acid. For most of the amino acids, there is more than one three letter codon. For example, GGU,GGC,GGA, and GGG all code for glycine. The three "nonsense" codons (UAA, UAG, and UGA) apparently signal the system to end the protein chain.

The final steps in the protein synthesis involve a **transfer RNA** (tRNA) molecule. The transfer RNA molecule is relatively small compared to the messenger RNA molecule. It carries a base triplet on one end that is complementary to the base triplet on the mRNA. The triplets form hydrogen bonds to each other, thus attaching the tRNA to the mRNA. Attached to the other end of the tRNA, there is an amino acid residue that corresponds to the base triplet on the mRNA. To begin the protein a second tRNA must come up to the adjacent triplet on the mRNA. When the two are adjacent the two amino acid residues join to begin the polypeptide chain. The process continues with the tRNA molecules moving along the mRNA template, each time adding a new amino acid to the protein, until a nonsense triplet appears. Then the process ends; the protein has been synthesized.

Now consider the error in the beta-chain of hemoglobin that causes sickle cell anemia. Since the beta-chain contains 146 amino acid residues, the strand of messenger RNA must have at least 3 x 146 = 438 bases. Since the error in the protein was at the 6th position, the error in the base sequence is in one or more of

the 16th, 17th, or 18th positions in the DNA sequence that codes for the beta-chain. The codes for glutamic acid and valine are:

Glu	Val
GAA	GUA
GAG	GUG
	GUC
	GUU

Clearly, the G in position 16 is the same for both Glu and Val. But in position 17, to change Glu to Val we must replace A by U. With GU preceding, any of the bases in position 18 will code for Val.

RECOMBINANT DNA TECHNOLOGY

I) human insulin

Among the remarkable things that can be done using modern biochemical techniques is to excise a complete gene from one DNA molecule and insert it in another DNA molecule. The program cites the example in which the gene coding for human insulin has been excised from a sample of human DNA and inserted in the DNA of the common microorganism, E. coli. The modified E. coli are cultured in a vat and busily set about synthesizing human insulin. In the past, diabetics used animal insulin obtained by grinding up and extracting animal organs, now human insulin synthesized in a factory by microorganisms is available.

There has been, and still is, considerable controversy over the use of recombinant DNA technology. While not all the conceivable possibilities of recombinant DNA technology are as benign as the human insulin synthesis, nonetheless the insulin example makes it clear that the technique should not be condemned in its entirety.

HANDS ON

1. *Using the table of mRNA codes in the book, write the amino acid sequence corresponding to the base sequence given below.*

   CUUUAUCGAACCAUU

QUESTIONS

1. *If the base sequence of one strand of the DNA molecule is*

   C A T G A G

   write down the base sequence in the complementary DNA strand.

2. *For the base sequence given in question 1, write the base sequence in the complementary RNA.*

3. *How many polypeptide chains are in the hemoglobin molecule?*

4. *There are 81 amino acid residues in the precursor molecule of bovine insulin. What is the* **least** *number of bases that must be in the DNA chain that codes for this molecule?*

5. *Insulin is a single molecule having two polypeptide chains connected by disulfide bonds. How many levels of structure does the insulin molecule have?*

UNIT 25

CHEMISTRY AND THE ENVIRONMENT

BEFORE WATCHING

YOU ALREADY KNOW

All the needed terms, concepts, and skills.

READ

Chapter 17: "Impact of Hazardous Wastes on Water Quality"

OVERVIEW

When we observe Nature, we see a number of grand cyclical transformations of elements. The nitrogen in the air is changed by special bacteria into nitrogen compounds usable by plants and animals. The waste materials from plants and animals are transformed by other bacteria back into elemental nitrogen. In plants carbon dioxide and water are made into carbohydrates and oxygen by photosynthesis. Animals eat the plants and breathe the oxygen; in this way they burn the carbohydrates, reconverting them to carbon dioxide and water. In the wild, animals die; their bodies decay and are used as nutrients by plants and microrganisms. These observations give new force to the ancient warning: "Remember man, that thou art dust and unto dust thou shalt return." Nature even recycles limestone, to dissolve it using flowing underground water and then reconstitute it as stalactites and stalagmites in the magnificent limestone caves.

These great cycles can tolerate some input from artificial sources without noticeable disruption. On the other hand, large amounts of foreign substances may produce disturbances in these natural cycles that cannot be corrected in a practical length of time.

This program focuses on the problem of chemical wastes. In the past, it was customary simply to dump them in rivers or pits, or vent the gases to the atmosphere.

Today these methods are no longer acceptable. It is necessary to clean up some of the waste dumps that were used in the past.

The program treats how and why waste is generated, and outlines a few of the methods that are being used to reduce and clean up waste.

A waste dump is used to show how different people view the same problem. An expert on carcinogens, a toxicologist, and a group of people who live near the dump comment on the hazards posed by the presence of the dump. The psychological and political aspects of the problem become evident. Finally, we see that all would agree that it ought to be cleaned up, but for quite different reasons.

New attitudes on the part of industry for reducing waste are illustrated.

WHAT TO LOOK FOR

THE PLANET AS A CLOSED SYSTEM

a) cyclical transformations
b) waste in chemical manufacturing

COST BENEFIT IDEA

c) pollution and biological productvity

CHEMICAL WASTE DUMPS

d) differing perceptions of risk

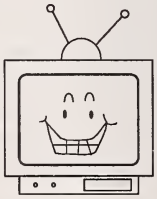
METHODS OF CLEANING UP

e) incineration
f) bioremediation

WASTE REDUCTION

g) process management and design
h) beneficial use of byproducts

WATCH THE PROGRAM



AFTER WATCHING

THE PLANET AS A CLOSED SYSTEM

a) cyclical transformations

In nature we observe certain ways in which elements are transformed in a cyclical way. For example, we inhale oxygen and exhale carbon dioxide. Green plants on land and microorganisms in the oceans use the carbon dioxide in photosynthesis, which produces carbohydrates and oxygen. Without this continuous recycling of carbon dioxide and generation of oxygen, we would soon exhaust the atmosphere's oxygen and suffocate.

The presence of humans and other animals is integrated into the balance of this natural cycle. But humans use tools which magnify their actions. And as the population grows, many more actions are magnified. Our giant industrial plants make all the wonderful things that we have become accustomed to in our modern world. But these industrial plants are also examples of how greatly mechanized manufacturing processes can magnify our actions. Not only do we have many more of the good things that the plant produces, but we have much more of the undesirable material, waste. Because of the gigantic size of modern industries, we are capable of damaging our environment beyond the ability of Nature to undo the damage within a practical length of time.

The question is whether we can reverse the damage that has been done or, at least, whether we can arrange matters so that we do much less damage in the future.

b) waste in chemical manufacturing

The fundamental law of chemistry is that mass is conserved. This means that if substances A,B, and C are required in the reaction to produce the desired substance, X, we could write the chemical equation

$$A + B + C \longrightarrow X$$

This means that the mass of X produced is equal to the total mass of A, B, and C used in the reaction. Unfortunately, life (and chemistry) is not so simple. With a given set of reactants, A, B, and C, and a prescribed set of processing conditions, it is rare that only one product is produced; ordinarily, we must write the reaction as

$$A + B + C \longrightarrow X + Y$$

where X represents the desired product(s) and Y represents all the other substances that are produced. The substance(s) Y may be necessary byproducts in the main reaction that produces X, or Y may be produced by side reactions that go on along with the main reaction. In either case, unless the substances Y are useful, they wind up as chemical wastes.

The existence of the substances Y implies that less of the desired product is produced from given amounts of A, B, and C. This costs the manufacturer in two ways. First, less product means less income; second, the more waste the more it costs to get rid of it. Thus, today it is becoming more important from the standpoint of economics to minimize waste.

The term "recycling" is used in several senses. It can mean something as simple as melting down scrap aluminum cans to produce new aluminum in a useful form or reprocessing waste paper to produce new paper, often of lower quality. More generally, it can simply mean the conversion of any waste material into something useful.

COST-BENEFIT IDEA

c) pollution and biological productivity

During World War II when DDT was introduced, it was hailed as the salvation of mankind from insect-borne diseases, particularly typhus. Today its use is prohibited in most Western countries because of its disastrous effects on wildlife, particularly waterfowl. The polychlorinated hydrocarbons, to which class both DDT and the PCBs belong, are generally a treacherous class of compounds. They tend to be carcinogenic, they often produce adverse effects on the central nervous system (Kepone is another example.) and, of course, DDT produced the fragility in the eggshells of birds. These compounds are relatively stable, so they do not decompose easily; they are nonpolar and so they accumulate in fatty tissue and thus stay in the food chain of animals.

In the Peter Raven interview, the idea of applying cost-benefit analysis to the manufacturing problem is suggested as a way to guide the future decisions on what to manufacture and to what uses a substance could be put. One of the costs to be counted would be any damage to biological productivity; the beneficial use of the material would be weighed against the costs. Decisions would have to be made case by case.

CHEMICAL WASTE DUMPS

d) differing perceptions of risk

The interviews with Bruce Ames, the parishioners of St. Martin de Porres church, and Halina Brown highlight the different ways of viewing the problem of chemical waste dumps.

Bruce Ames, an authority on carcinogens, sees a lack of hard evidence of risk and from his experience with carcinogens tends to doubt that the waste dumps pose a high risk. The parishioners who live near the dump are obviously convinced that many of their illnesses are a result of the presence of the dump. Halina Brown, the toxicologist, points out that the fears of the parishioners are real, even though they may not be based on scientific evidence. She points out that there is a tremendous gap between how a scientist perceives the risk and how those who are exposed to the risk perceive it. The problem of chemical wastes has psychological and political dimensions as well as the scientific ones. Being knowledgeable on the subject would be useful even for those who are emotionally involved in the problem. Even so, the fact that the world is full of natural carcinogens may not be reassuring to most people and clearly would not be so to the parishioners in the interview.

METHODS OF CLEANING UP

e) Incineration

One of the classical methods of getting rid of wastes, or at least reducing their volume, is by incineration, that is, by simply burning them. Oil refineries formerly simply "flared off" waste combustible gases without even attempting to use the heat released for other purposes. This was acceptable in the days of cheap oil. Today the incineration process can not only be used to reduce wastes but the energy released can be put to use.

The phrases "to reduce waste" or "get rid of waste" must not be taken too literally. Our options in dealing with waste are severely limited by the fundamental law of chemistry, the law of conservation of mass. Suppose we have 25 kilos of waste; what can we do with it? Only four things.

Do nothing; leave it where it is.

Cover it over and hope that no one notices.

Repackage it. Confine it in such a way that it is no longer offensive or a threat and so can be tolerated either where it is or somewhere else. Note that since the "package" weighs something, the waste plus the package now weighs more than 25 kilos.

React it with something else to convert it either to something useful or to something less offensive. ("Recycling" falls in this category, as does incineration.) The recycling of scrap aluminum, of waste paper, and of scrap iron are examples of the best that can happen. The aluminum can be melted

down and most of it recovered to make new useful aluminum items. Even so, unless we use solar energy to melt the aluminum, some new "waste" appears from the burning of fuel to heat the furnace. Incineration has the advantage that it converts a carbonaceous waste that you can see into a gas that you can't see. Unfortunately, the gas, carbon dioxide, now pollutes the atmosphere and contributes to the greenhouse effect. Also, every 12 kilos of carbon produces 44 kilos of carbon dioxide, so the pile of waste is now heavier.

Incineration of waste today is much more complicated than simply touching a match to it. The machinery must be designed to trap harmful materials, such as metals.

f) bioremediation

Although the word bioremediation is a relative newcomer to our vocabulary, the process to which it refers is as old as life itself. It refers to the transformation of wastes into relatively harmless materials by letting bacteria or other organisms feed on it. An example is termites and micro-organisms feeding on the deadwood in the forest, or bacteria converting leaves into humus in the composting process. Sewage treatment plants have traditionally used a fermentation process to convert the solid wastes into a material that is like humus and is nearly odorless. So, Nature has provided examples of the use of micro-organisms to transform materials from one form to another.

Recently much effort has gone into the development of micro-organisms that can transform organic wastes that are not commonly used as foodstuffs for microbes. Micro-organisms have been developed that will feed on petroleum-like materials. It is hoped that these will be useful for cleaning up petroleum spills as well as waste dumps. Much more needs to be done in this area.

WASTE REDUCTION

g) process management and design

Since the disposal of industrial wastes has become a much larger problem today than it has been in the past, it is obvious that one of the best ways to cope with the problem is to generate as little waste as possible. Substantial savings can be realized by aggressive management to reduce waste, as exemplified by the valve testing regime shown in the program. If the valve leaks one of the reactants, stopping the leak increases the yield of product; if the valve leaks product, every bit saved contributes to increased profit. These savings are leveraged by the elimination of the cost of waste disposal.

In the future we can expect more attention to be paid to the design of the process and the equipment with the aim of minimizing waste. This will usually be done when new plants are being designed and built. A little of this may be possible with existing plants, but major remodelling of an existing plant can be extremely costly.

h) beneficial use of byproducts

The program cites the example of branched-chain polypropylene as a byproduct in the manufacture of straight-chain polypropylene, the usual white product. Presently the branched-chain material is burned as fuel; the hope is to convert it to a putty-like material that can be used as a caulk. Also, cloudy batches of the regular product can be sold to users that do not need a high-clarity product.

HANDS ON

1. *Look through the trash basket in the kitchen of your home. Estimate the percentage of the trash that is i) paper, ii) plastic, iii) metal, iv) glass. Which of these classes of materials, in your opinion, could be recycled with the most benefit?*

QUESTIONS

1. *Name at least two benefits of recycling more of our wastes.*

2. *One chemistry teacher said, "The first law of chemistry is, 'You can never throw anything away.'" That is true. Consider what alternatives are available in dealing with chemical wastes.*

3. *What are the pros and cons of incineration as a method of reducing waste?*

4. *Can we really reduce waste? What does it mean to reduce waste?*

5. *According to one of the interviewees in the program, celery and mushrooms contain carcinogens. Will you stop eating celery and mushrooms? How will you decide whether or not to eat them?*

UNIT 26

FUTURES

BEFORE WATCHING

OVERVIEW

Having looked at what chemistry has accomplished in the past, and many of the current chemical achievements, it is appropriate to close the series with a view of the future. The program is designed to provide some understanding of the directions in which chemistry may go in the next few decades. This program consists of a series of interviews with outstanding chemists from both the academic and the industrial worlds.

Generally, the program is organized in four segments. The first deals with the new techniques and instruments that will be available in the future, such things as the new super microscopes, laser techniques, scanning devices, and computer applications.

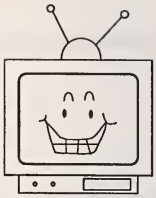
The second segment deals with the chemistry involved in developing new materials for practical applications. For example, the research and development of composite materials is still in its infancy; the graphite-fiberglass tennis racquet is an example. The development and use of superconducting materials is just beginning.

The third segment deals with the synthesis of new molecules and determination of their structure. Strange new molecules, such as dodecahedrane, have no obvious use now but which are important in understanding the limits within which covalent bonds can be formed. New drugs may be designed to be more specific in their action, with fewer side effects. The architecture of proteins will be greatly clarified, helping us to better understand the way they function.

The fourth segment deals with biotechnology and genetic engineering. These technologies can legitimately be regarded as extensions of organic chemistry. They hold out the promise of producing totally new varieties of plants that are resistant to various insects and diseases. The ultimate possibility of curing hereditary diseases may be realized with these techniques.

Finally, the challenge of doing these things is emphasized, as is the necessity of doing them within the constraints of sound environmental policy.

WATCH THE PROGRAM



AFTER WATCHING

'It was so kind of you to come!
And you are very nice!'
The Carpenter said nothing but
'Cut us another slice.
I wish you were not quite so deaf --
I've had to ask you twice!'

— **Through the Looking Glass, and What Alice Found There**
-- Lewis Carroll

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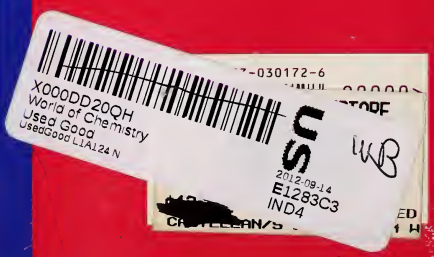
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